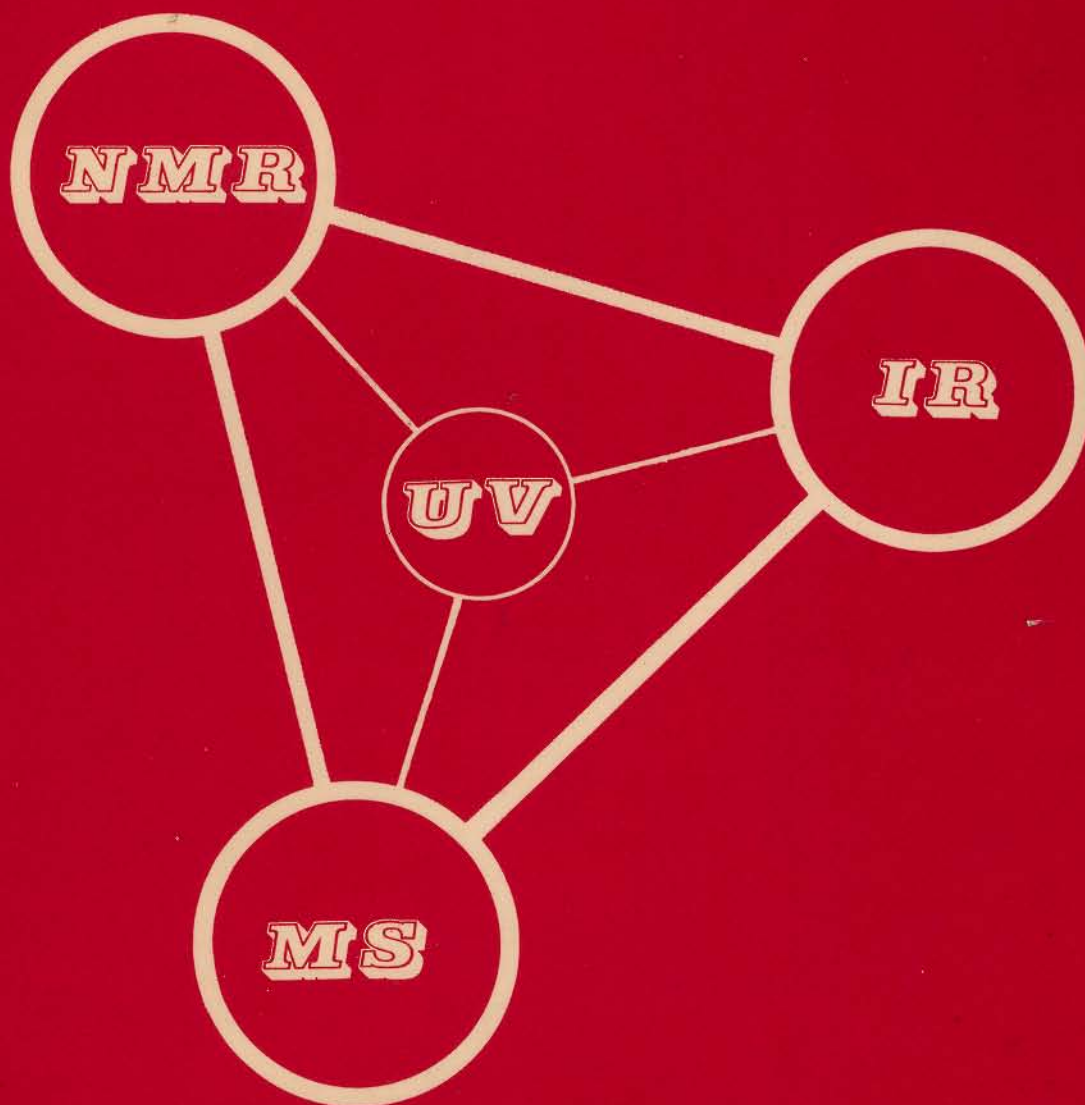SPECTROSCOPY
IN
EDUCATION
Volume 2

SPECTROSCOPIC
TECHNIQUES
IN
ORGANIC CHEMISTRY

A. J. Baker
T. Cairns

Spectroscopy In Education Series

T. CAIRNS
Editor

SPECTROSCOPY IN EDUCATION

Volume 2

Spectroscopic Techniques

in

Organic Chemistry

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University of Glasgow

by R.A. Raphael, F.R.S.,
Regius Professor of Chemistry, The University of Glasgow.

In this department the practical teaching in the final undergraduate year is used to provide the student with a grounding in modern research techniques. The recent publication of a series of spectroscopic problems in organic chemistry used in this training has elicited both favourable comment and enquiries for further details of the course itself. To meet this demand Dr. Baker and Mr. Cairns have arranged for the publication of the practical manual devised by them for this course. The manual is designed to provide the student with a succinct digest of the basic theoretical and practical aspects of the four branches of spectroscopy most used in organic chemistry and to give guidance in their intelligent usage for structural assignment.

There is no doubt that the ready availability of such a compilation has made the teaching much more efficient from the student point of view and I hope that future users will benefit from the authors' hard work as much as we have done.

Department of Chemistry,   R.A. RAPHAEL
The University,
Glasgow, W.2, Scotland.
April, 1965.

In modern chemical research the information obtained by the various branches of spectroscopy (namely, IR, NMR, MS and UV) plays a major role in structural determinations. The combination of four such methods provides the practicing organic chemist with a vast amount of the information required for the structural elucidation of a molecule. This manual sectionalizes the four branches of spectroscopy under consideration. The introductory sections remind the student of the basis of each method, the experimental sections of the techniques of applied spectroscopy, and the various correlation tables of the important frequencies and values associated with each method. The final sections are devoted to the interpretation of series of spectra. A suggested bibliography for further study is also included.

We would like to express our warmest thanks to our colleagues in this department for their willing help and co-operation at all times. We are deeply indebted to Dr. A. Melera (Varian AG, Zurich) for his kind permission to reproduce the NMR spectra used in the interpretation scheme.

Our final thanks are reserved for Prof. R.A. Raphael, F.R.S., who, besides contributing a Foreword, offered continuous personal encouragement during the preparation of the manuscript.

Department of Chemistry,   A.J. Baker
The University,   T. Cairns
Glasgow, W.2.
April, 1965.

AUTHORS' NOTE TO SECOND EDITION

The decision to prepare a second edition rather than continue reprinting the first was motivated by two factors. In the first instance, the many reviews and personal letters received indicated that this practical manual fulfilled a great need in the teaching of applied spectroscopy. Secondly, it was generally agreed that revision in certain sections would increase its usefulness. It must be emphasised, however, that this volume is not a textbook and is meant to be employed in conjunction with a practical course in spectroscopy.

October, 1966   A.J. Baker
                                                                            T. Cairns

ACKNOWLEDGEMENTS

CONTENTS

In a polyatomic molecule, the atoms are not rigidly linked together and thus have the ability to vibrate from the rest position. For a molecule with n atoms, there are, in space, 3n coordinates and therefore 3n – 6 degrees of freedom to describe the fundamental internal vibrations since of the 3n coordinates, three degrees of freedom must be deducted for translation and three for rotation. In the case of linear molecules only two coordinates are required to describe the rotational mode and therefore the number of degrees of freedom for internal vibrations is 3n – 5.

The energy required to increase the amplitude of vibration of chemical bonds is of the order of 5 kcal./mole and is provided by radiation in the infrared region (400 to 5000cm^{-1}) and the near infrared or "overtone region" (5000 to 12500cm^{-1}). Absorption of infrared radiation causes the excitation of the molecule to higher vibrational levels and is quantized. The spectrometer measures this absorption at each frequency and produces an infrared spectrum. However, classical electrodynamics specifies that the excitation of a particular normal vibration in a molecule must obey two conditions. Firstly, the normal vibration must have the same frequency as the electromagnetic radiation and secondly, a change in the magnitude and direction of the dipole moment must also occur. Some modes of vibration will not absorb infrared radiation since no change in dipole moment will occur. Hence $\nu_{C \equiv C}$ of acetylene is inactive as the bond is symmetrically substituted. (This infrared inactive vibration may appear in the Raman spectrum where the selection rules are different).

The concept of vibrational excitation may be exemplified by comparison with a process in acoustics. If two identical tuning forks (i.e. they vibrate with exactly the same frequency) are set up within a short distance of each other and one is sounded, one can soon observe that the second fork begins to ring. This is due to the fact that the vibrations from the first fork excite the air and cause it to vibrate at the same frequency. These atmospheric vibrations in turn excite the second tuning fork to vibrate at the same frequency. The air between the two forks acts as the coupling mechanism for the exchange of vibrational energy from one to the other.

In infrared spectroscopy the conditions are analogous. Here the vibrating systems are the electromagnetic radiation and the atoms in the molecule; the dipole moment is the coupling mechanism. The radiation transmits its vibration to the dipole which in turn excites the molecular vibrations at the same frequency. Thus absorption of radiation occurs.
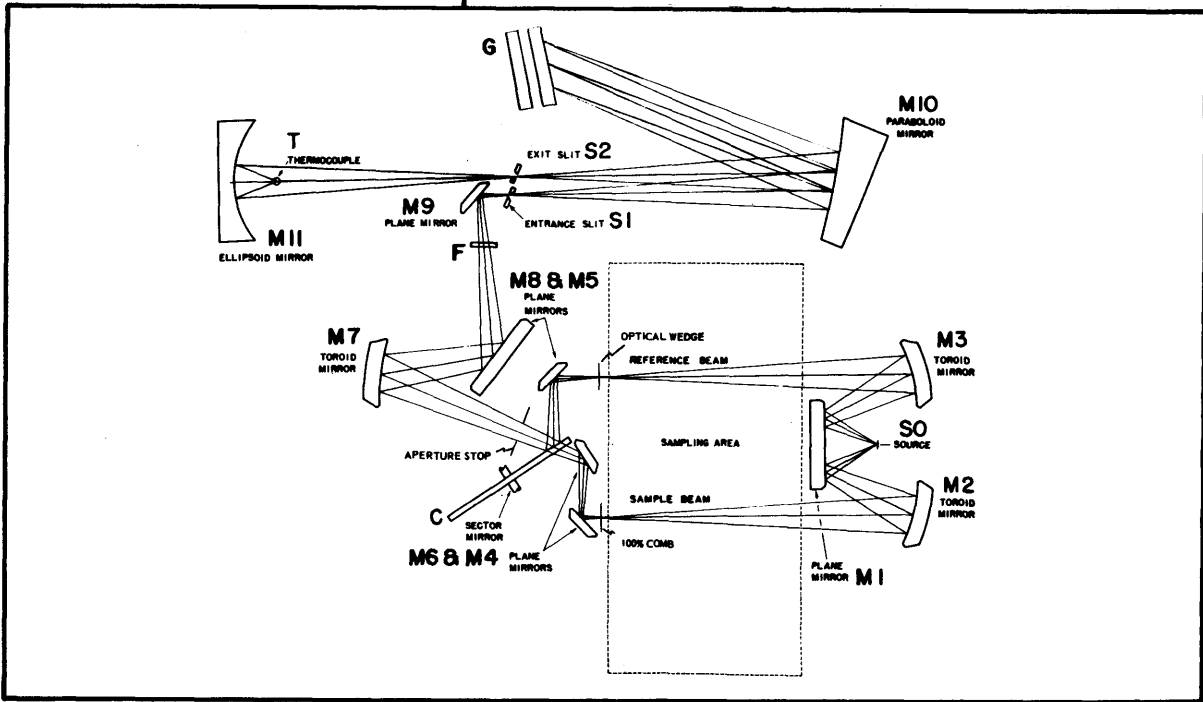
Since each different chemical bond in the molecule has a different dipole moment, absorption of radiation will occur over a range of frequencies. Thus, if infrared radiation of successive frequencies is passed through a substance, a series of absorption bands is recorded – the active fundamental modes of vibration. These are of the following type:

<div style="text-align:center">

ν Stretching
δ Bending (in plane)
γ Bending (out of plane)
τ Twisting
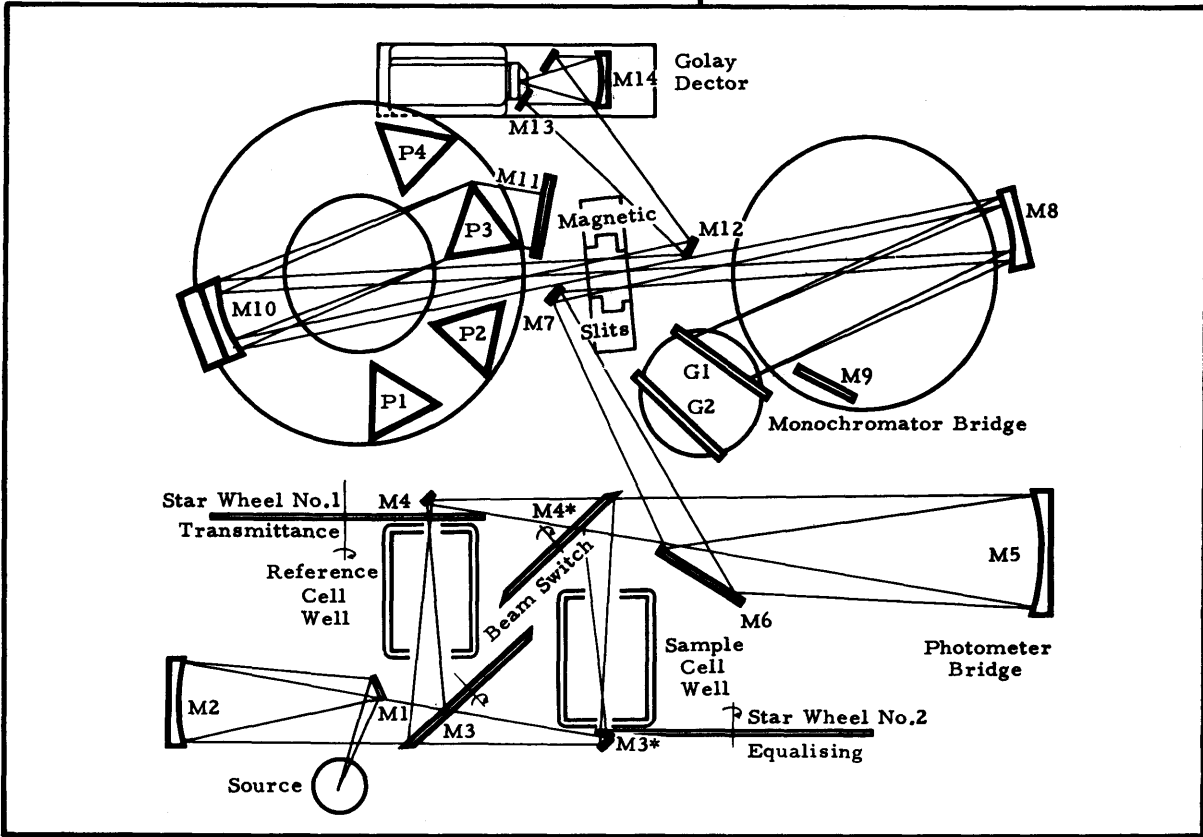ρ Rocking
ω Wagging

</div>

Apart from the fundamental vibrations, harmonic and combination vibrations may also occur. The harmonic vibrations possess frequencies which represent approximately integral multiples of the fundamental frequency. The frequencies of the combination vibrations are composed of the sum of, or the difference between, the frequencies of two or more fundamental or harmonic vibrations.

If the origin of the infrared spectrum is kept in mind it is apparent that the spectrum presents a wealth of information of the basic characteristics of the molecule, namely, functional groups and their spatial arrangements. It is for this reason that the infrared spectrum is often referred to as the "finger print of the molecule".

Optical layout of the
PERKIN-ELMER Model 237 Grating Spectrophotometer

Optical layout of the
UNICAM SP.100 Spectrophotometer

Experiments

Commercial infrared spectrometers are capable of a good wavenumber or wavelength accuracy; but it is essential to know how far the indicated frequency values are in fact away from the true values. There are many reasons why a spectrometer should indicate frequency values different from the correct ones; but, in the main, it is due to very slight imperfections in the cam controlling the Littrow mirror movement, or in the various linkages controlling grating movement.

Spectrometer calibration should be carried out fairly frequently and this is best accomplished by using standard substances, the spectra of which have been fully investigated and the band frequencies accurately recorded.

The International Union of Pure and Applied Chemistry (I.U.P.A.C.) has recently issued "Tables of Wavenumbers for the Calibration of Infrared Spectrometers". These provisional values are the best that can be produced from existing data. This book provides a comprehensive survey of the problem.

The usual substances involved in spectrometer calibration are polystyrene, ammonia gas, hydrogen chloride gas, water vapour, and indene. Ammonia gas, hydrogen chloride gas, water vapour are normally used for the larger, more sophisticated instruments whilst polystyrene and indene are used for the smaller instruments.

Experimental

Record the spectrum of a polystyrene film and that of indene (0·025mm thickness).

After recording the spectra, plot the values of (standard minus observed) wavenumber (+ or -) against observed wavenumber. This gives a calibration graph.

Standard Wavenumbers

Polystyrene

907, 1028, 1069, 1154, 1181, 1451, 1494, 1603,
1802, 1871, 1944, 2851, 2924, 3027, 3055cm^{-1}

Indene

693, 718, 830, 861, 915, 947, 1019, 1068,
1123, 1166, 1205, 1226, 1288, 1312, 1361, 1393,
1458, 1553, 1610, 1915, 1943, 2771, 2887, 3068cm^{-1}

Record the spectra of ammonia gas, hydrogen chloride and water vapour. Measure up the spectra and using the standard values listed below plot the calibration curves over these regions.

Ammonia gas

792, 816, 848, 868, 888, 892, 908, 912,
952, 972, 1008, 1027, 1046, 1065, 1085, 1103,
1122, 1141, 1159, 1177, 1195cm^{-1}

Hydrogen chloride

2906, 2926, 2945, 2963, 2981, 2998cm^{-1}

Water vapour

1617, 1636, 1653, 1663, 1669, 1696, 1717, 1740,
1757, 1762, 1785, 1793cm^{-1}

3566, 3586, 3629, 3650cm^{-1}

Due to the high absorption characteristics of many organic compounds in the infrared region, very short path length cells are employed, and to utilise the Beer-Lambert relationship, these path lengths must be determined with some accuracy. One of the best ways is by the interference fringe method.

Theory and Calculation

The trace obtained will have the appearance shown in (a) whilst (b) represents a section (greatly exaggerated) through a cell of thickness t.

(a)

(b)
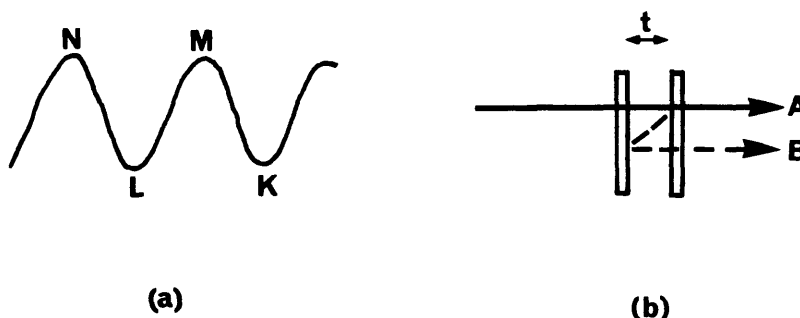
If a beam of radiation of wavelength λ is incident on one face and perpendicular to it most of the radiation will pass straight through (beam A) but some will emerge having suffered a double reflection at the inner surfaces (beam B). The wave form of B will have been retarded by a distance equal to 2t relative to beam A. If the retardation 2t is equal to a whole number of wavelengths n (where n is a positive integer) then A and B will be in phase and there will be a slight increase in intensity (e.g. points such as K and L in the diagram). Similarly there will be a slight decrease in intensity when the two beams A and B are out of phase - that is when $2t = (n + \frac{1}{2})$ e.g. points such as M and N.

If λ_1 be the wavelength of a maximum of intensity K and λ_2 be the wavelength of the next minimum M then the following equations are true:-

$$2t = n\lambda_1$$

$$2t = (n + \tfrac{1}{2})\lambda_2$$

Eliminating n

$$2t = [2t/\lambda_1 + \tfrac{1}{2}]\lambda_2$$

Converting to wavenumber

$$\nu'_1 = 1/\lambda_1 \, cm^{-1} \text{ and } \nu'_2 = 1/\lambda_2 \, cm^{-1}$$

Multiplying through by 2

$$4t\nu'_2 = 4t\nu'_1 + 1$$

or

$$t = \frac{1}{4[\nu'_2 - \nu'_2]} \, cm$$

Thus it is only necessary to measure the wavenumber of a maxima and minima and find their average separation to calculate the cell thickness. The accuracy depends on the wavelength calibration of the spectrometer and is almost independent of the cell thickness.

If the windows have poor surfaces or are badly aligned, it may be impossible to observe interference fringes.   It may also be difficult to measure fringes accurately on cells greater than 0·5mm in thickness.

Alternative methods of calibrating cells include:

1. Use of a travelling microscope focussed first on one face and then the other.

2. Measurement of the absorption of a standard substance whose extinction coefficient is accurately known.

3. Comparison of the absorption of a standard substance in the cell with that of the same standard in a variable path length cell which has been calibrated at smaller path lengths.

It should be emphasized from the outset that there is no "correct" way to polish a rock salt plate. Each worker should use the technique which his own experience shows to give the best results in his or her particular case.

"Expert" polishers differ considerably in their preferred techniques, but the following basic principles should be followed:

A rock salt polishing kit should be obtained containing:

1. A glass block with roughing lap on one side and smoothing lap on the other. The smoothing lap should be slightly convex to counteract the tendency to wear away the edges of the rock salt surface more than the centre.

2. A polishing lap covered with fine polishing velvet.

3. A bottle of absolute alcohol, saturated with salt by keeping a few chips or crystal in the bottle.

4. A sponge for cleaning the laps frequently. Laps soon become coated with a deposit of salt which scratches the surface of the plate being polished.

5. A supply of surgeons' finger cots or rubber gloves for handling plates.

Rough cut plates may be polished on the roughing lap, using a lubricant. Use a rotatory polishing movement and clean the glass surface frequently using a slightly moist sponge. This should be continued until a uniformly matt surface has been obtained. Plates purchased commercially are normally polished to this stage.

The smoothing lap may then be employed, using a lubricant. The plate should be held in different positions in the fingers from time to time in order to obtain an even finish.

The final polishing is carried out on the velvet lap using a little polishing rouge, and a few drops of alcohol. Finish by polishing on a clean section of the velvet.

The spectrum of a non-volatile liquid may be scanned by a very simple "liquid sandwich" technique. In this, the liquid is trapped, as a very thin film, between rock salt plates.

Experimental

1. Take a clean, polished rock salt plate and lay it flat on a "Kleenex" tissue.

2. With a glass rod, or dropping tube put one or two drops of the liquid to be examined on the surface of the rock salt plate.

3. Place the other rock salt plate on top using a wedging technique, viz. touch the side of the lower plate nearest to the liquid with one side of the upper plate, then pivoting about this point place the upper on the lower. This drives the test liquid forward thus excluding air bubbles.

4. Press down gently to produce an even film.

5. Transfer this "sandwich" to a suitable cell mount and place in the spectrometer.

6. Run the spectrum from 650 - 4000cm^{-1}. This should have one or two peaks in the 5 - 10% transmission range and a few in the 85% transmission range. Note that a single rock salt plate in the reference beam often causes the transmission to rise by 5 - 6%.

7. After running satisfactory spectra with the first liquid, demount the cell, wash the windows with chloroform and dry gently (by dabbing - not rubbing) with Kleenex.

8. Mark upon the spectra you so obtain, the frequencies of the principal peaks, and the structural assignments you make to them.

Place one drop of Nujol (medicinal liquid paraffin) onto a polished rock salt plate and press out to a thin film with another polished plate. A slightly rotating movement should be used in order to obtain an even, bubble-free film.

Run this spectrum of pure Nujol.

Place about 5mg of sample into a clean dry agate mortar, and grind vigorously for some minutes until it is finely powdered. Then add one drop of Nujol and grind again. When the mixture is of the same consistency as heavy motor oil or light vaseline, transfer it on to a rock salt plate and squeeze it into a uniform layer as previously described with pure Nujol.

Run this spectrum and decide which peaks are due to the sample and which to the Nujol.

If the sample absorption is too high, the film may be made thinner by squeezing the rock salt plates closer together, or by regrinding the sample with one more drop of Nujol. The principle should be adopted, however, of having only as little Nujol as is necessary to obtain a fluid, evenly-distributed "mull".

Fibrous or waxy solids are difficult to grind into a suitable suspension. The former may be pretreated by gently rubbing the sample between two roughened agate plates to cut the fibre across its axis. Ground glass plates also serve for this purpose, but small particles of glass may be introduced into the mull and show absorption bands in the $1000cm^{-1}$ region. These particles could also cause abrasion of the windows. Waxy solids may sometimes be suspended satisfactorily by prolonged grinding with the mulling agent. Failing this, the addition of a small quantity of powdered alkali halide, or the chilling of the sample may make it more tractable for the mulling process.

Quantitative analysis of mulled specimens has been carried out by using an internal standard technique. A weighed amount of an inert compound with one, or at the most two, well defined infrared absorption peaks is mulled with a known weight of a sample and the absorption of the latter is measured relative to that of the standard. The most widely used standards are relatively simple compounds such as calcium carbonate, lead thiocyanate or sodium azide. It should be emphasized, however, that this method demands a highly reproducible mulling technique.

Should it be desired to study frequency ranges in which Nujol itself absorbs, other mulling agents may be considered. Fluorolube (perfluorokerosene, a mixture of fluorinated hydrocarbons) or hexachlorobutadiene may be employed. The former, however, is difficult to remove from the plate surfaces and sample recovery is troublesome.

Alkali halide salts, particularly potassium bromide and potassium chloride can be "fused" to clear glasses at room temperature in vacuo at a pressure of 15 - 30 tons/sq. in.   Any solid intimately mixed with the halide before pressing is held in the clear or relatively clear disc and its spectrum may be obtained since the alkali halide shows little or no absorbance over the range covered. The literature is extensive and although the method is attractive it is essential to realise that a number of difficulties may arise (see DUYCKAERTS, Analyst, 84, 201) and it is unwise to make assignments solely on alkali halide disc spectra.

Experimental

1. Place about 1 mg of sample into a clean dry agate mortar, and grind vigorously for some minutes until it is finely powdered.

2. Weigh out 300mg of the alkali halide, and add gradually to the mortar, constantly mixing and grinding with the sample.

Preparation of Die and Punch

The component parts should be kept warm in an oven (60°) to prevent condensation on the surfaces and subsequent disc fogging.

Assemble the die:

1. Hold the barrel vertically in one hand.

2. Place the anvil in the barrel (from the top as held).

3. Slide the die body downwards over the barrel and anvil until completely home.

4. Invert the assembly and stand it on a clean bench.

5. Pour the powder prepared above onto the face of the anvil.

6. Insert the plunger gently into the barrel and holding the barrel firmly in place with the index and middle fingers of the left hand, keep rotating the plunger to spread the powder evenly over the anvil.

7. Whilst rotating the plunger, gently draw it up a little and then complete its withdrawal very gently (the plunger usually fits into the barrel with little clearance so that sudden withdrawal causes a partial vacuum disturbing the powder).

8. Insert the platten, polished side down into the barrel.

9. Place the vacuum ring in its indent in the die body, and insert the plunger through the flat disc top (tight fit due to its vacuum ring).

10. Put the plunger on top of the platten in the barrel and let their combined weight carry the platten down as far as it will go.   Now with finger pressure press the flat die top onto the neoprene ring in the die body.   Press also upon the plunger to ensure a good tight fit.
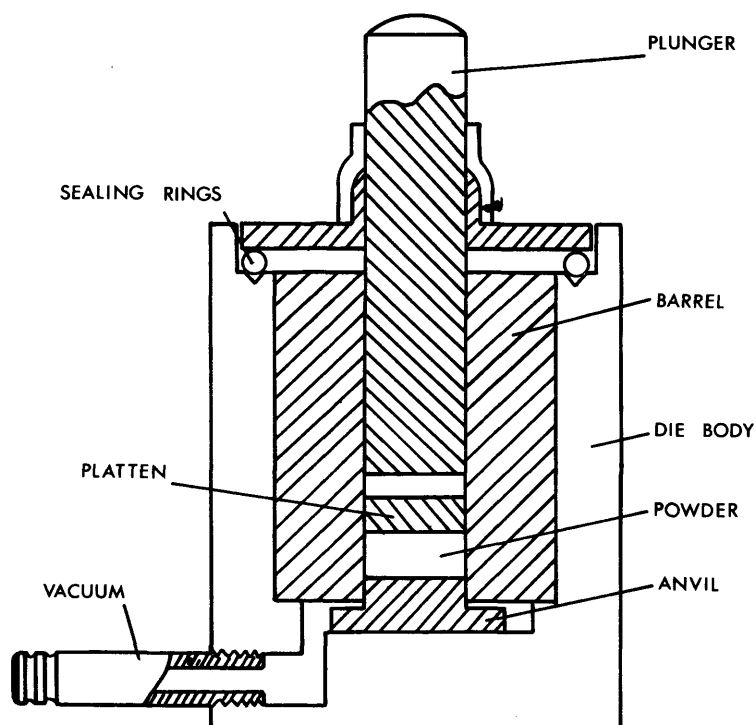
Die and Punch

Pressing the Disc

1. Connect the die to a vacuum line (about 1mm is required) and evacuate for 30 seconds.

2. Maintaining the vacuum, place the die on the base block of the hydraulic press and apply a total pressure of 10 - 15 tons for 4 minutes.

3. Release the vacuum slowly and then the pressure. Remove the die from the press.

4. Remove the die body and the plunger/die top from the barrel assembly.

5. Place the barrel assembly, anvil uppermost on the bench and very carefully ease the anvil out of the barrel with the flat blade of a screwdriver. The disc should now be visible but it must be removed from the die barrel.

6. Replace the plunger/die top assembly in the barrel and the die body back over the barrel, i.e. original assembly but without the anvil.

7. Holding the die assembly upside down in the left hand with the plunger projecting between the index and middle fingers and the weight held in the palm of the left hand, place the disc upside down in the press holding it carefully as described.

8. Very gently pump the hydraulic press handle so as to push the plunger, platten and disc through the barrel. A sudden increase in weight on the hand indicates that the disc has been released from the barrel.

9. Remove the die body, pick off the disc. Mount in the disc holder of the spectrometer and run the spectrum from 650 - 4000cm^{-1}. Mark and assign the peaks.

In the past, the height of a particular peak has been found to vary from one infrared spectro-meter to another, and also with spectrometer conditions. These experiments are designed to demonstrate the effect of two important variables which cause this, viz. scanning speed and resolving power. Resolving power depends on the optical dimensions of the monochromator and on the type of prism or grating used: for any given monochromator it varies with slitwidth.

Scanning Speed - Examination of Records

It should be noted that the peaks are higher when a slower rate of scan is used. The error due to fast scanning is greater with sharper peaks.
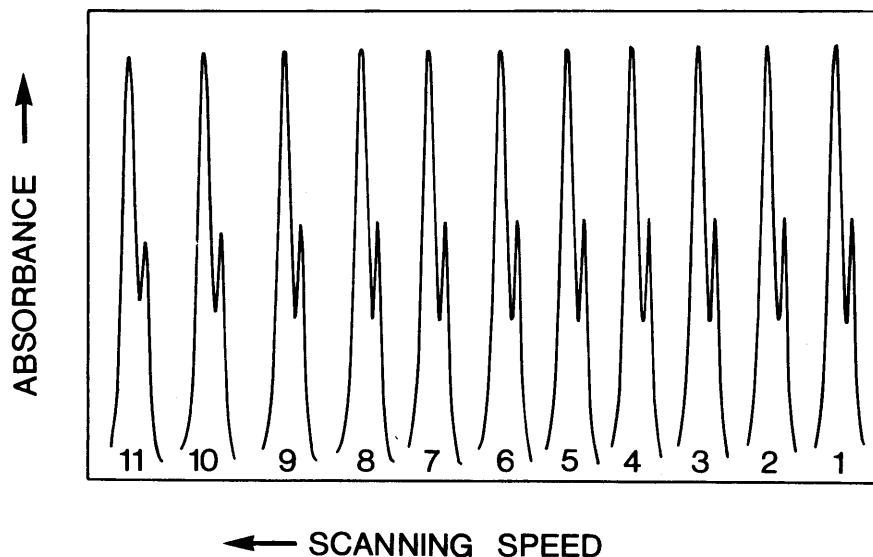
← SCANNING SPEED

Effect of Scanning Speed on the 1601cm^{-1} Band of Polystyrene

For quantitative analysis spectra must be scanned more slowly than is necessary for qualitative work. The same scanning speed must be used for measuring the standard solution when cal-ibrating and the unknown solution.

When an attempt is made to transfer data from one spectrometer to another the scanning speed must be such than running more slowly does not increase the height of the peak.

Resolving Power

Measure the frequency $[\nu]$, halfband width $[\Delta\nu_{\frac{1}{2}}^{a}]$ and apparent extinction coefficient $[\varepsilon^{a}]$ of the fundamental stretching vibration of the carbonyl group in phenyl benzoate run on the Unicam SP.100 with

        (a) Grating in use

        (b) Prism with narrow slits, and

        (c) Prism with wide slits
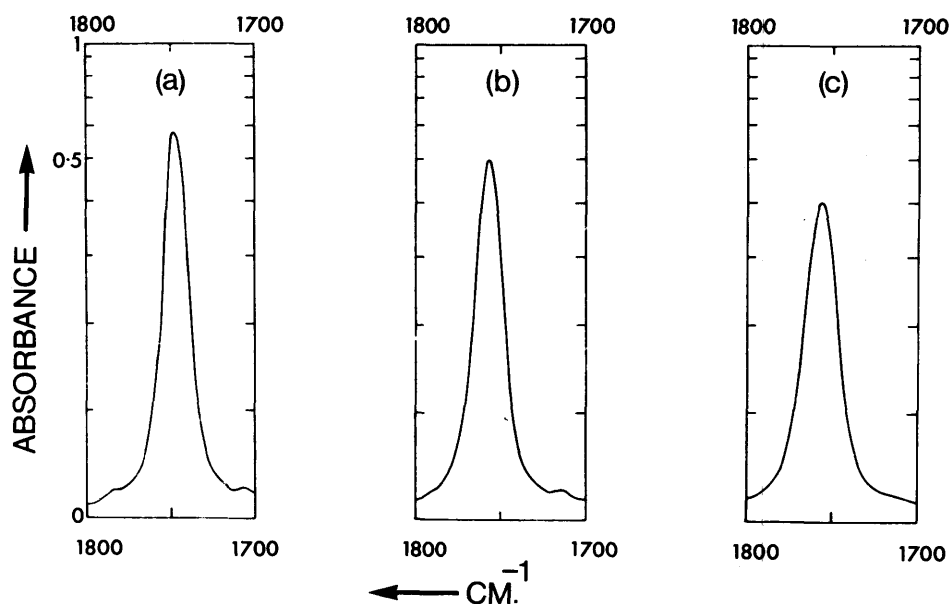
To calculate the halfband width $[\Delta_{\frac{1}{2}}^{a}]$ measure the width of the peak in cm^{-1} at the value of optical density obtained by O.D./2 + base line.

The apparent extinction coefficient $[\varepsilon^{a}]$ is given the following relationship:

$$\varepsilon^{a} = \text{O.D./molarity} \times \text{cell path in cms.}$$

Examination of Records

Note that the peaks are highest with the grating in use, lower with the prism and narrow slits, and lowest with the prism and wide slits. It should also be noted that the area under the peak does not change.

When carrying out an analysis the same slitwidth must be used for recording the spectra of the unknown and the calibration solutions. If possible, resolving power high enough to give no slitwidth error should be used, although, in general, only grating spectrometers will give this.

In the past the effect of slitwidth (i.e. limited resolving power) on infrared spectrometers has prevented the transfer of data from one instrument to another. To a large extent grating spectrometers have removed this difficulty in infrared spectrometry.

Solution techniques are commonly employed in infrared spectroscopy. The main difficulty lies in the selection of the solvent. Most solvents have strong absorption characteristics in their own right and so these peaks will be super-imposed upon those of the solute. Solvents most commonly employed are carbon tetrachloride, chloroform, cyclohexane, carbon disulphide, acetonitrile, tetrachloroethylene etc.

Spectroscopically pure solvents are desirable, "AnalaR" grades are nearly always acceptable without further treatment, other grades should be purified by chromatography or by distillation.

Three points must be noted:

1. Some solvents pick up atmospheric water so affecting hydroxyl band intensities. Solvents may be dried over zeolite molecular sieves (25g. per winchester). Chloroform must be dried by passage through silica gel before use. This operation is best carried out just before use.

2. Some solvents decompose on standing.

3. The actual shape and position of bands drawn in solution spectra require careful consideration due to the possibility of solvent-solute interaction.

It is often convenient to utilise the pure solvent in the reference beam at the same thickness in the sample beam. This leaves the solute peaks alone (except in those regions where the solvent absorbs so strongly that no energy remains in either beam and the pen does not receive any signal).

Experimental

1. Obtain, from the Demonstrator, a fixed path length cell, filled with the solvent. Run the spectrum of this over the region 650 – 4000cm^{-1}.

2. Record the (solvent-solvent) spectrum over the range 650 – 4000cm^{-1}, i.e. solvent in both beams.

3. Empty the fixed path cell by removing the Teflon plugs and blowing dry air through the cell. Refill the cell with the solution under test as instructed under A to F below. Note the concentration of this solution. Replace the cell in the spectrometer.

4. Now plot the (solvent-solution) spectrum over the range 650 – 4000cm^{-1}. Mark and assign the peaks.
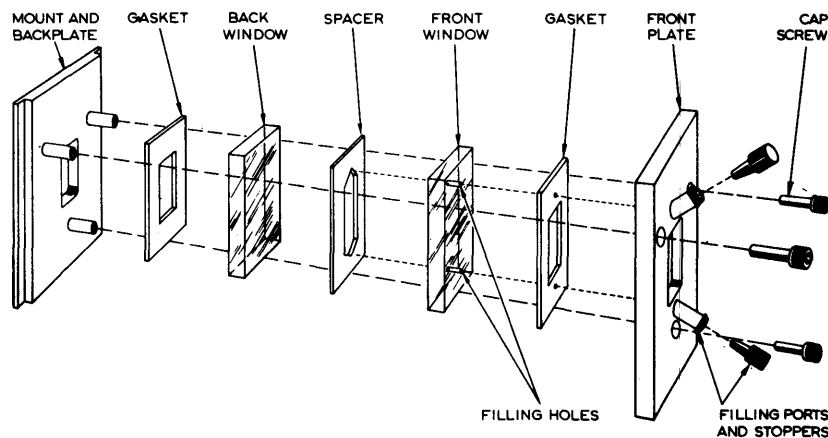
Construction of a Liquid Cell

Filling the Cell

The filling ports of the usual fixed cells will take a hypodermic syringe (Luer type) directly to give a tight seal.

A. Take up the liquid sample in a hypodermic syringe. Remove both Teflon stoppers from the cell and holding it in the left hand insert the syringe nose into the top port and wash the cell through with the solution, catching the washings in a beaker. Repeat this once or twice until the cell has been cleaned with the solution under examination.

B. Now hold the cell at bench level slightly inclined upwards from the vertical and holding a Teflon stopper in the fingers of the left hand.

C. Fill the hypodermic syringe with solution and insert the syringe nose this time into the bottom port. Very gently inject the solution into the cell, observing it through the rock salt windows.

D. When the upper port is seen to be filling with the liquid and no air bubbles are visible in the cell, press home the Teflon stopper into this port making a liquid-tight joint.

E. Remove the syringe from the lower port and place a Teflon stopper into this one as well.

F. Wipe any drops of solution from the cell plates immediately with tissue before placing in the spectrometer.

NOTE: After recording the spectrum, the empty syringe may be used to blow out the solution through the filling port. As soon as possible wash the cell thoroughly with a good amount of pure solvent and then blow dry air through the cell.

Production of Calibration Curve

Quantitative work in the infrared, as in the visible and ultraviolet portions of the spectrum, is founded upon the Lambert-Beer (or Bouger-Beer) law which may be written

$$O.D. = \varepsilon . c . l.$$

where $O.D. = \log I_0/I = \log 1/\text{transmission} = \log 100/T\%$

  c = concentration

  l = path length in cm.

  ε = apparent extinction coefficient (a constant)

A plot of O.D. with concentration should be linear if Beer's law is obeyed and this calibration curve is of great importance in quantitative analysis.

In this case, a calibration curve for naphthalene in cyclohexane is to be prepared and several standard solutions should be prepared. Cyclohexane is a useful solvent for the study of aromatic absorptions over the range $650 - 850 \text{cm}^{-1}$ and scans over this range only will be required.

Experimental

1. Obtain from a Demonstrator a fixed path length cell and fill it with cyclohexane.

2. Place the cell in the sample beam of the spectrometer and examine the trace over the range $650 - 850 \text{cm}^{-1}$. Adjust the 100% T control upon the instrument until the plot over most of this range lies between 90 and 100% T (Absorbance $0\cdot05 - 0\cdot0$).

3. Record the spectrum of cyclohexane alone from $650 - 850 \text{cm}^{-1}$.

4. Do not remove the chart paper. Now empty the cell and refill it with the weakest naphthalene solution. Record the spectrum of this solution over the same range on the same chart paper.

5. Repeat 4 with all other solutions.

Treatment of Results

The dotted line represents the pure solvent, the full line the solution spectra in this case.
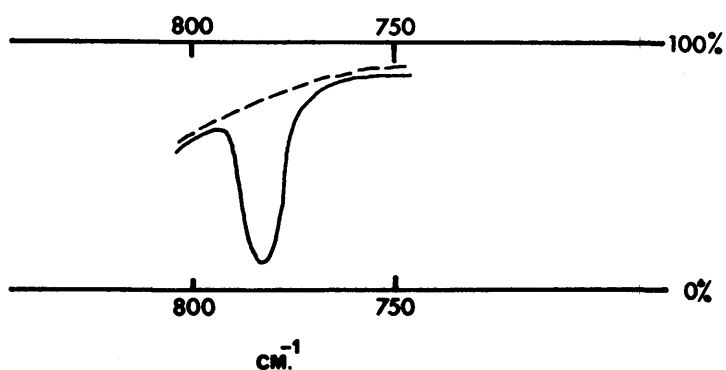
At the peak wavenumber, read the value of % T (solvent) and t (solution). Then, correcting for solvent, the optical density of the solution is given by

$$\log[100/t] - \log[100/T] = A$$

Where absorbance paper has been used then this value is given by a simple subtraction.

$$\text{Absorbance soln.} - \text{Absorbance solvent} = A$$

Plot A versus concentration of naphthalene in each solution. The result should be linear and pass through the origin. This is the calibration curve.

Commercial xylene may be analysed qualitatively for its isomers by comparison of its infrared spectrum with reference spectra of the pure compounds.

From the qualitative spectra, suitable bands or spectral regions are selected for a quantitative analysis. The concentrations of o-, m-, and p-xylene will then be determined quantitatively by application of the base-line measuring technique and working curves to the unknown and standards.

Experimental

Prepare the following standard solutions:

(a) Standard solution I containing 1ml o-xylene, 15ml m-xylene and 6ml p-xylene made up to 100ml with cyclohexane.

(b) Standard solution II containing 5ml o-xylene, 7ml m-xylene and 3ml p-xylene made up to 100ml with cyclohexane.

Obtain the infrared spectra of both standard solutions in the same 0·05mm sodium chloride cell over the range 840 – 670cm^{-1}. The zero % transmission must be accurately determined.

Apply the base-line technique to calculate the optical densities of the absorption bands at 794cm^{-1} (p-xylene), 741cm^{-1} (o-xylene) and 690cm^{-1} (m-xylene) for both spectra.

Plot a Beer's Law curve (optical density against concentration) for each of the three wavelengths from the data for the two standards.

By means of the working curves from Beer's Law determine the exact concentrations of the isomers in the unknown commercial sample.

Theory

By Beer's Law, the optical density D_{mix} of a mixture is the sum of the optical densities D_1 and D_2 of the mixture's components 1 and 2, i.e. at one fixed spectral frequency in a two-component mixture

$$D_{mix} = D_1 + D_2 = \epsilon_1 c_1 l + \epsilon_2 c_2 l$$

where ϵ_1 and ϵ_2 are the extinction coefficients of components 1 and 2 at that frequency, l is the path length (cm) and c_1 and c_2 are the concentrations of 1 and 2.

If at the frequency chosen for measurement of D_{mix}, one component absorbs strongly (i.e. ε_1 is large) and the other only weakly (i.e. ε_2 is almost zero) then the equation for D_{mix} becomes

$$D_{mix} = \log_{10} I_0/I = \varepsilon_1 c_1 l$$

Hence a plot of $\log_{10} I_0/I$ against concentration will be roughly a straight line. This line is called a 'working curve' for the analysis of component 1. Likewise component 2.
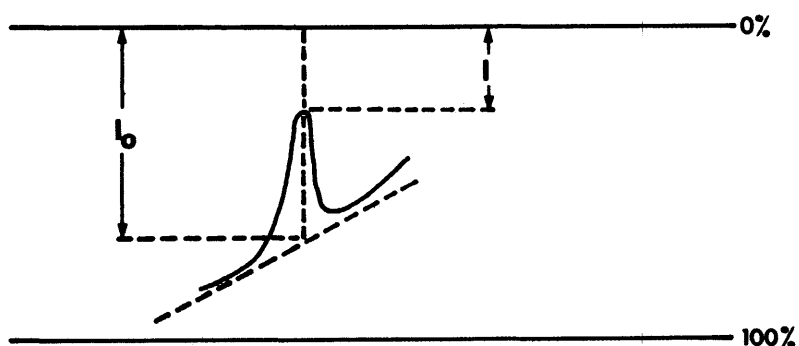
Since the beginnings of infrared spectroscopy, it has been recognised that the hydroxyl group gives rise to a band around $3600\,cm^{-1}$ due to its fundamental stretching vibration. Perhaps the most convenient feature of this fundamental stretching frequency, $\nu(OH)$, is that it behaves as an isolated vibration in a region of the spectrum which is populated by relatively few other absorptions. Thus infrared spectroscopy is well suited to detection of hydrogen bonding. There are a number of proton donating groups such as O-H, N-H, -CONH, and -SH whose participation in a hydrogen bond can be detected by this convenient tool.

The subject of hydrogen bonding has been a topic which has received a great deal of attention during the last two decades and the present state of knowledge is excellently summarized in Pimentel's and McClellan's book. In general, a hydrogen bond can be formed with a group that possesses a lone pair or pairs of electrons. The characteristic feature of the presence of hydrogen bonding involving a hydroxyl group is that the fundamental stretching frequency, $\nu(OH)$, and its harmonics are shifted to a lower frequency.

In the structural diagnosis of hydroxylic compounds, therefore, it is of the utmost importance to be able to determine precisely the exact frequency, shape and strength of the hydroxyl stretching frequency, $\nu(OH)$. At this juncture, however, it is necessary to point out that two quite different types of hydrogen bond exist, namely, intermolecular and intramolecular. Intermolecular hydrogen bonding, as the name suggests, is achieved by participation between molecules, either the same, i.e. $X-H\cdots X-H\cdots X-H$, or different, i.e. $X-H\cdots Y-$; while intramolecular hydrogen bonding is that bonding occurring within the same molecule possessing the hydroxyl function or proton donor involved in that bond.

In general, therefore, it is extremely satisfactory to study the hydroxylic compound in dilute solution where, with increasing dilution, the polymers break up first to dimers and finally to monomers. To achieve such a condition where intermolecular hydrogen bonding is negligible it is necessary to carry out a concentration dependence study to determine the conditions at which only intramolecular hydrogen bonding is operative. Such conditions are normally attained by working at concentrations less than 0·01 M in carbon tetrachloride, a solvent which is virtually transparent in the hydroxyl stretching region.

Intramolecular hydrogen bonding has certain steric consequencies arising from its predominantly electrostatic nature, for significant intramolecular hydrogen bonding can only occur if the two electronegative centres are sufficiently close to one another. The classical example of conformational elucidation solely from intramolecular hydrogen bonding is that of cis-1:3-diol. This molecule must be retained in a diaxial conformation, [I], by the hydrogen bond.

2·64 Å   [I]   [II]   3·3 Å
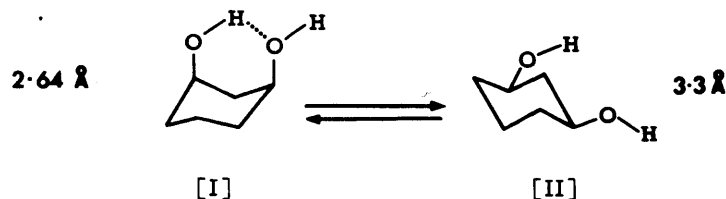
The OH$\cdots$O distance of [II] was too large to permit the hydrogen-bonded hydroxyl observed in the dilute carbon tetrachloride solution of this compound.

Experimental

Examine by infrared spectroscopy the hydrogen bonding in

       1. Benzoic acid

       2. Cyclohexanol

       3. o-Hydroxydiphenyl

Discuss the nature of the bonding in each case.

The resolution of a prism instrument falls off as the frequency increases. Spectral slit widths and spectral band widths approach one another at high frequencies so that bands appear broad, and where close, merge into one another. The high resolution available in instruments fitted with gratings is of particular advantage in this connection.

Free O-H stretching vibrations are to be observed about $3600 cm^{-1}$ but the exact location depends upon the type of OH group involved. In this experiment the high resolution of the P.E. 237 is utilised to demonstrate the presence of both primary and tertiary alcoholic groupings in a mixture.

Experimental

Prepare three solutions as follows:

1. Primary alcohol in CCl_4

2. Tertiary alcohol in CCl_4

3. Mixture of primary and tertiary alcohols in CCl_4

Record the spectrum of each solution. Compare records. If time permits, repeat these runs on a prism instrument.

Correlation Charts

The following section lists a series of tables of group frequencies which are useful in the interpretation of infrared spectra. An attempt has been made to present some of these as flow-sheet diagrams similar to those used in preparative organic chemistry to describe a particular synthesis. In this way the reader can observe the development and trend undergone by a particular group frequency when conjugation occurs, ring size alters, etc. The frequencies quoted are those recorded in carbon tetrachloride solution.
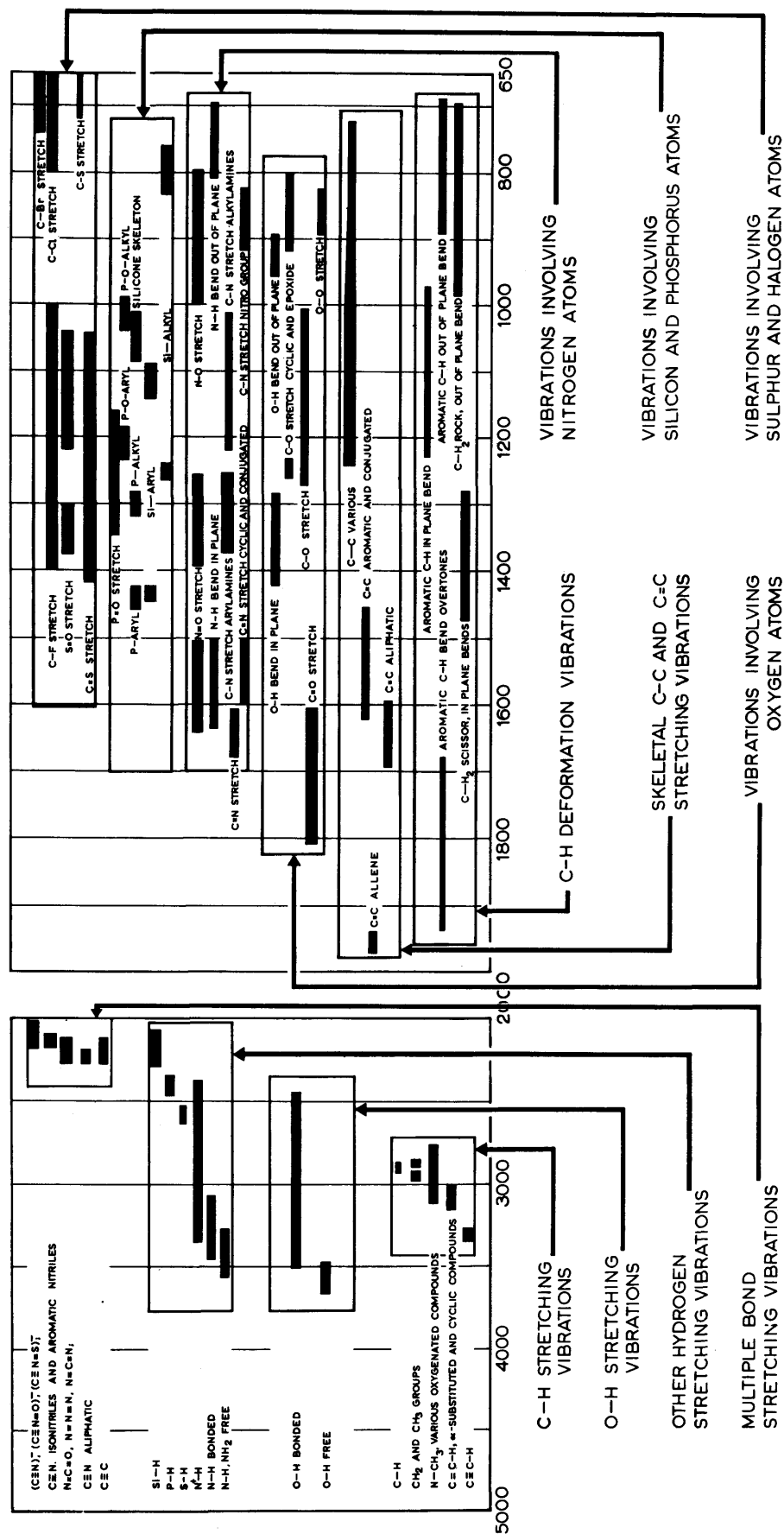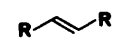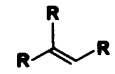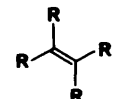
STRUCTURAL CORRELATION CHART

Frequency axis (cm⁻¹): 5000 — 4000 — 3000 — 2000 — 1800 — 1600 — 1400 — 1200 — 1000 — 800 — 650

Lower chart (left region, 5000–2000)

- (C≡N)⁻, (C≡N≡O)⁻, (C≡N≡S)⁻;
- C≡N, ISONITRILES AND AROMATIC NITRILES
- N=C=O, N=N=N, N=C=N;
- C≡N ALIPHATIC
- C≡C
- SI—H
- P—H
- S—H
- N⁺—H
- N—H BONDED
- N—H, NH₂ FREE
- O—H BONDED
- O—H FREE
- C—H
- CH₂ AND CH₃ GROUPS
- N—CH₃, VARIOUS OXYGENATED COMPOUNDS
- C≡C—H, α-SUBSTITUTED AND CYCLIC COMPOUNDS
- C≡C—H

Region labels (lower chart)
- C—H STRETCHING VIBRATIONS
- O—H STRETCHING VIBRATIONS
- OTHER HYDROGEN STRETCHING VIBRATIONS
- MULTIPLE BOND STRETCHING VIBRATIONS

Upper chart (2000–650)

- C—F STRETCH
- S=O STRETCH
- C=S STRETCH
- C—Br STRETCH
- C—Cl STRETCH
- C—S STRETCH
- P=O STRETCH
- P—ARYL
- P—ALKYL
- P—O—ARYL
- P—O—ALKYL
- SILICONE SKELETON
- SI—ARYL
- SI—ALKYL
- N=O STRETCH
- N—H BEND IN PLANE
- C—N STRETCH ARYLAMINES
- C≡N STRETCH CYCLIC AND CONJUGATED
- N=O STRETCH
- N—H BEND OUT OF PLANE
- C—N STRETCH ALKYLAMINES
- C—N STRETCH NITRO GROUP
- C≡N STRETCH
- O—H BEND IN PLANE
- C=O STRETCH
- O—H BEND OUT OF PLANE
- C—O STRETCH CYCLIC AND EPOXIDE
- C—O STRETCH
- O—O STRETCH
- C=C ALIPHATIC
- C=C VARIOUS
- C=C AROMATIC AND CONJUGATED
- AROMATIC C—H IN PLANE BEND
- AROMATIC C—H BEND OVERTONES
- AROMATIC C—H OUT OF PLANE BEND
- C—H₂ ROCK, OUT OF PLANE BEND
- C—H₂ SCISSOR, IN PLANE BENDS
- C=C ALLENE

Region labels (upper chart)
- C—H DEFORMATION VIBRATIONS
- SKELETAL C—C AND C=C STRETCHING VIBRATIONS
- VIBRATIONS INVOLVING OXYGEN ATOMS
- VIBRATIONS INVOLVING NITROGEN ATOMS
- VIBRATIONS INVOLVING SILICON AND PHOSPHORUS ATOMS
- VIBRATIONS INVOLVING SULPHUR AND HALOGEN ATOMS

- 24 -

	$-CH_3$	$\longrightarrow$	$-CH_2$	$\longrightarrow$	$-CH\genfrac{}{}{0pt}{}{CH_3}{CH_3}$	$\longrightarrow$	$-C\genfrac{}{}{0pt}{}{CH_3}{CH_3}CH_3$
ν	2962 2872		2926 2853		2890		2962 2872
δ_a	1460		1467		1460		1460
δ_s	1380				1385 1370		1395 1385 1365

	ν_{CH}	$\nu_{C=C}$	γ_{CH}
R⌒	3095–3075	1648–1638	990 910
R₂C=	3090–3075	1658–1648	890
cis R–CH=CH–R	3030–3010	1662–1652	690
trans R–CH=CH–R	3030–3010	1678–1668	980
R₂C=CH–R	3040–3010	1675–1665	840
R₂C=CR₂		1675–1665	

These originate from the motion of the hydrogen atoms out of the plane of the benzene ring. The number and position of the bands depends primarily upon the number of adjacent hydrogen atoms remaining on the benzene ring. The band patterns obtained are very characteristic and provide a useful tool in structural diagnosis of the substitution of the benzene ring. The symbols S and M refer to strong and medium absorptions respectively.
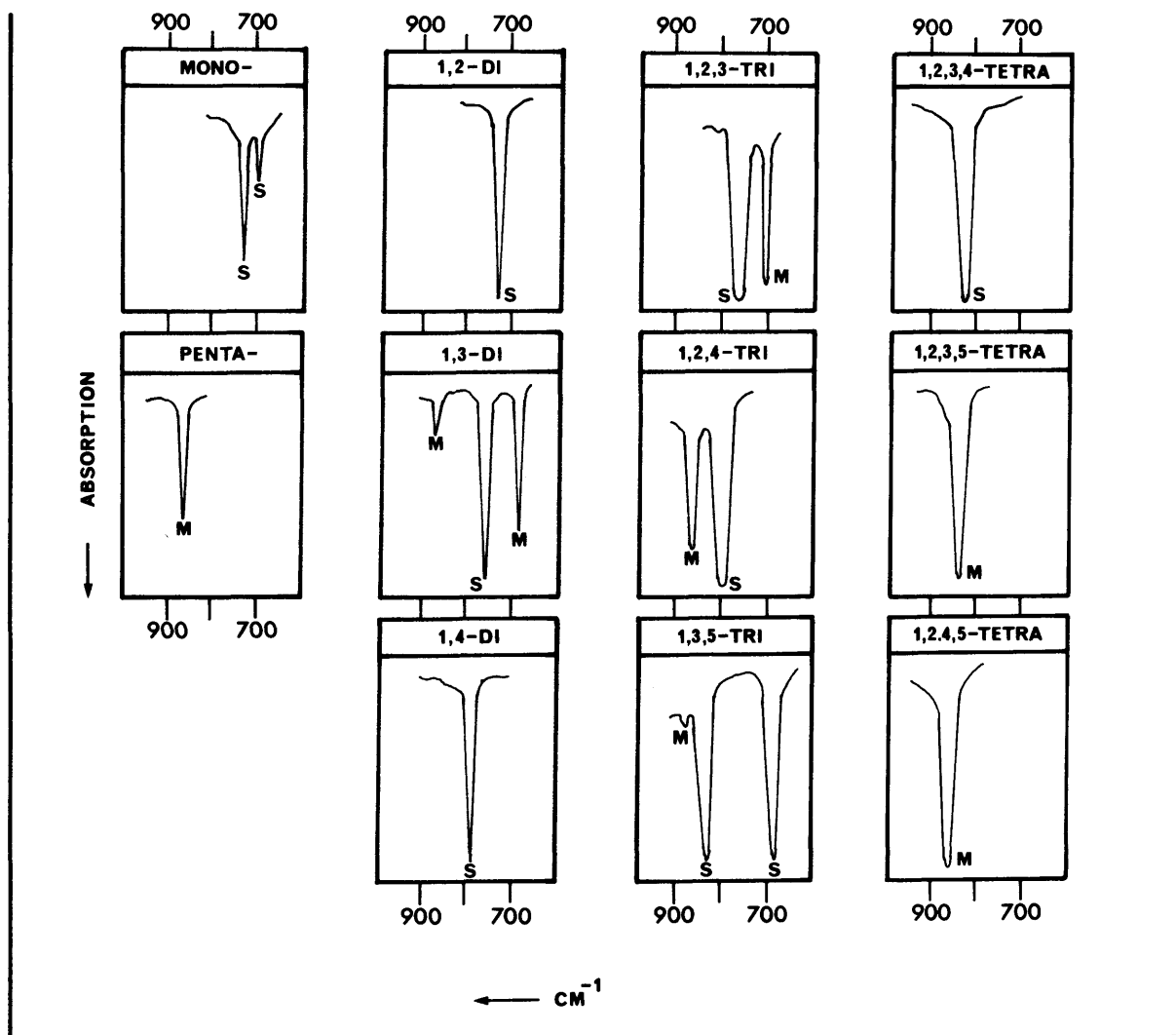
Hydroxyl groups easily form hydrogen bonds. Therefore the hydroxyl vibration, ν_{OH}, is strongly depressed in comparison with that in isolated molecules. This is seen in the infrared spectrum by a broadening of the hydroxyl band and a shift in the band maximum to lower frequencies. The values quoted in the table below have been recorded in dilute CCl_4 solution to avoid inter-molecular association, i.e. ν_{OH} (free).
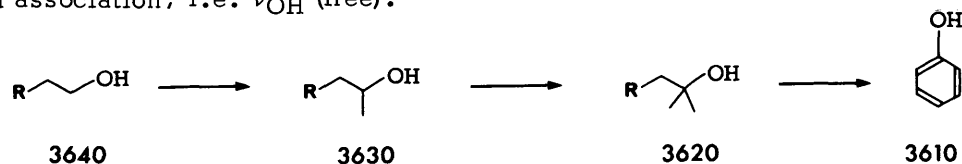
| 3640 | 3630 | 3620 | 3610 |

Carbonyl Stretching Frequencies

R 1725 → R 1685 → R 1675 → 1700

OR 1735 → OR 1720 → OR 1745

↓

O OR

KETO 1735
ENOL 1650

1735   1764   1719

1770   1800   1750

1826

1824   1802   1865   1848
1748   1761   1782   1790
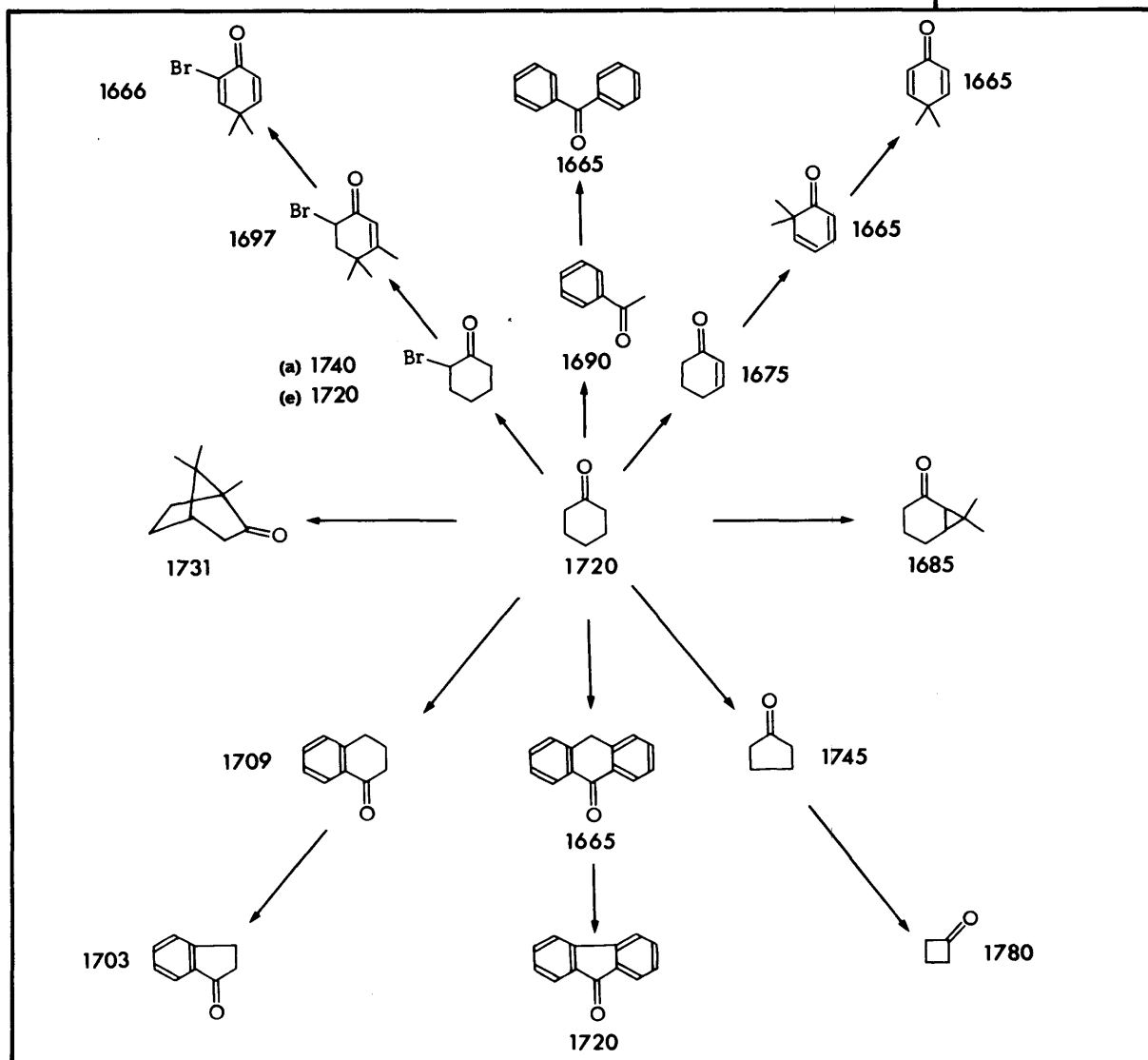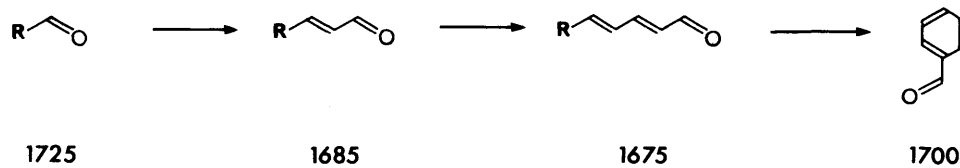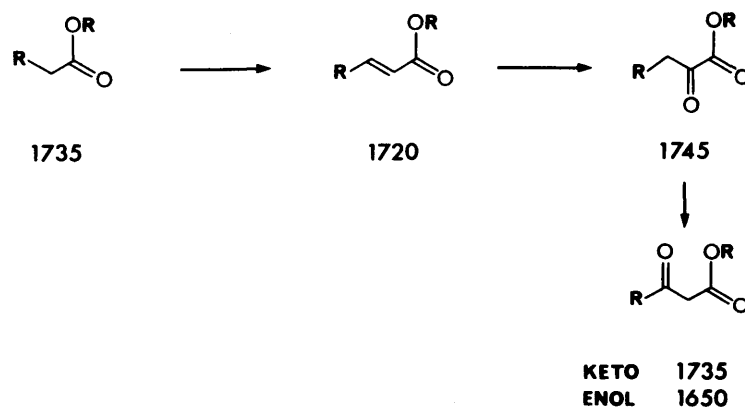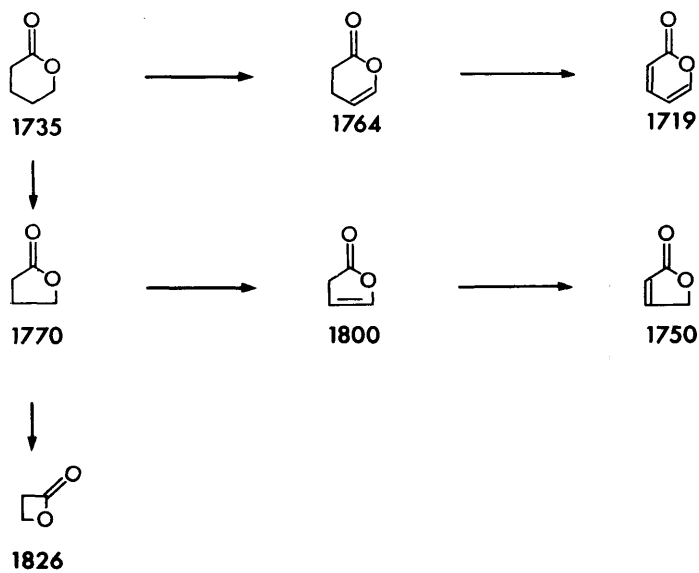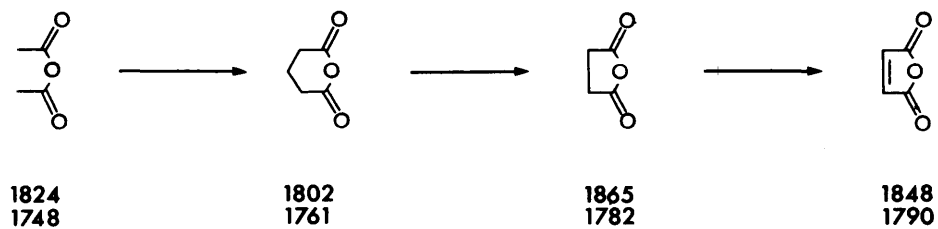
Interpretation of Infrared Spectra

The following set of infrared spectra (recorded as liquid films or KCl discs) illustrate the technique involved in the interpretation of a spectrum. In some cases, one can deduce the molecular structure of a molecule while in others only the basic functional groups can be identified and a guess made as to a possible structure.
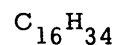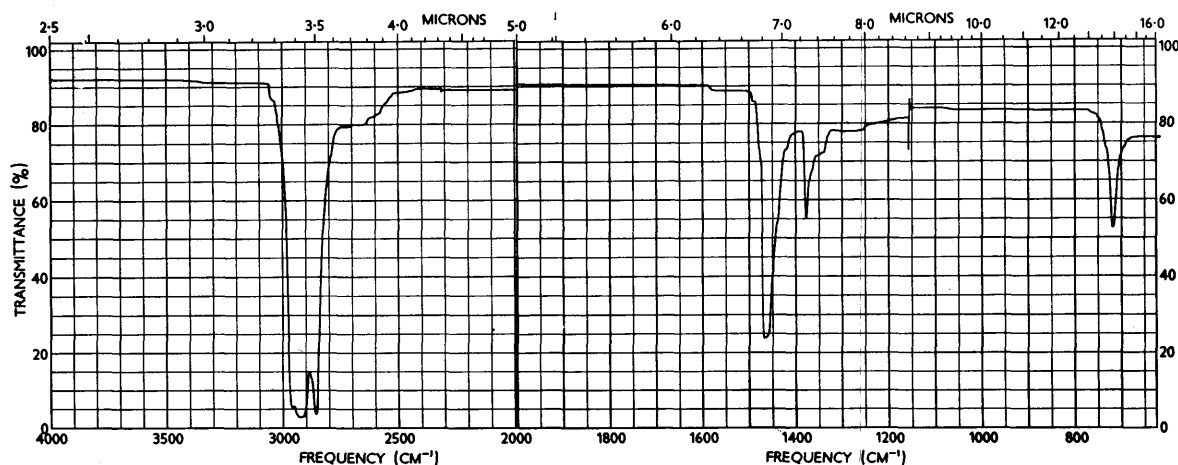
The ν_{CH} frequencies all lie below $3000 cm^{-1}$; an indication that the material is saturated, since unsaturated ν_{CH} frequencies always occur above $3000 cm^{-1}$. The molecular formula agrees with this finding, i.e. $C_n H_{2n+2}$. At $1480 cm^{-1}$ there appears two overlapping bands. These arise from the scissoring motion of CH_2 groups and the antisymmetrical bending mode of CH_3 groups. The symmetrical bending mode of CH_3 groups occurs at $1379 cm^{-1}$. The remaining band in the spectrum at $720 cm^{-1}$ is significant. This band arises from the rocking motion of CH_2 groups in a straight chain of five carbon atoms or longer. The absence of characteristic skeletal frequencies between 1300 and $750 cm^{-1}$ and the strength of the band at $720 cm^{-1}$ strongly suggest a straight chain paraffin. This substance is n-HEXADECANE.
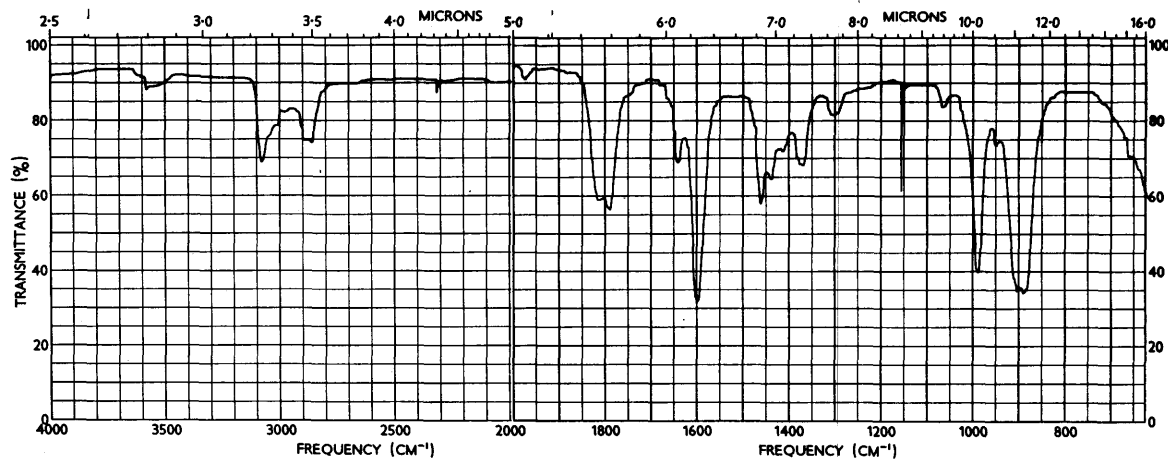
Bands above $3000 cm^{-1}$ suggest an olefin or aromatic structure. The presence of a carbon double stretching frequency at $1600 cm^{-1}$ and the γ_{CH} frequencies at 990 and $900 cm^{-1}$ point to an olefin. The molecular formula tells us we have two double bond equivalents, i.e. compound is a diene. This then explains the two $\nu_{C=C}$ bands at 1650 and $1600 cm^{-1}$. Where two double bonds are conjugated two frequencies result:- the out-of-phase stretching at $1600 cm^{-1}$ and the much weaker in-phase stretch at $1650 cm^{-1}$. The nature of the double bonds is determined from the γ_{CH} frequencies - 990 and $900 cm^{-1}$ for a vinyl group and $890 cm^{-1}$ for a terminal vinylidene group. The group of bands below $3000 cm^{-1}$ together with the deformation frequencies at $1380 cm^{-1}$ suggest a CH_3 group. The appearance of the band at $1800 cm^{-1}$ could be attributed to the first overtone of the band at approximately $900 cm^{-1}$. This substance is ISOPRENE.
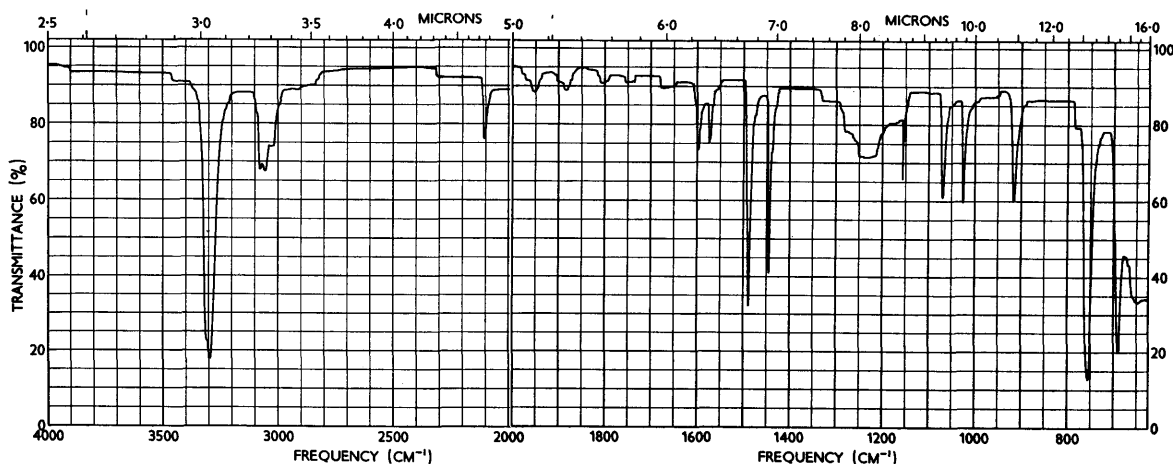
The sharp band at $3300cm^{-1}$ is characteristic of a terminal acetylene. The $\nu_{C\equiv C}$ frequency at $2100cm^{-1}$ confirms this finding. Aromatic skeletal vibrations appear at 1600 and $1500cm^{-1}$. A close inspection at the region 600 to $800cm^{-1}$ reveals the fact that the benzene ring is monosubstituted (γ_{CH} = 690 and $750cm^{-1}$). This is confirmed by the pattern of the overtones between 2000 and $1650cm^{-1}$. Since there are no bands corresponding to the ν_{CH} frequencies for CH_2 and CH_3 groups the substance is PHENYLACETYLENE.
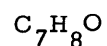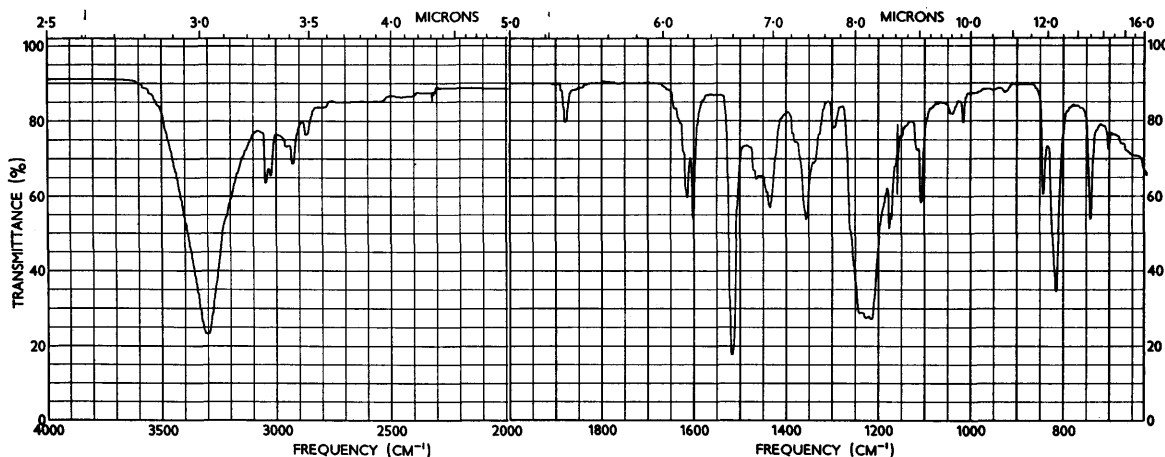
The broad absorption centred at $3300cm^{-1}$ suggests we are dealing with a hydroxylic compound (band due to intermolecular association). The $3000cm^{-1}$ region affords evidence for both unsaturation and a CH_3 group. Aromatic skeletal vibrations appear at 1600 and $1520cm^{-1}$, i.e. the compound is phenolic. The absorption band centred around $1230cm^{-1}$ is the carbon-oxygen single bond stretch, ν_{C-O}. The formula leads us to a cresol structure. The γ_{CH} frequency of $815cm^{-1}$ suggests a 1,4-disubstituted benzene. This substance is p-CRESOL.
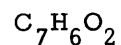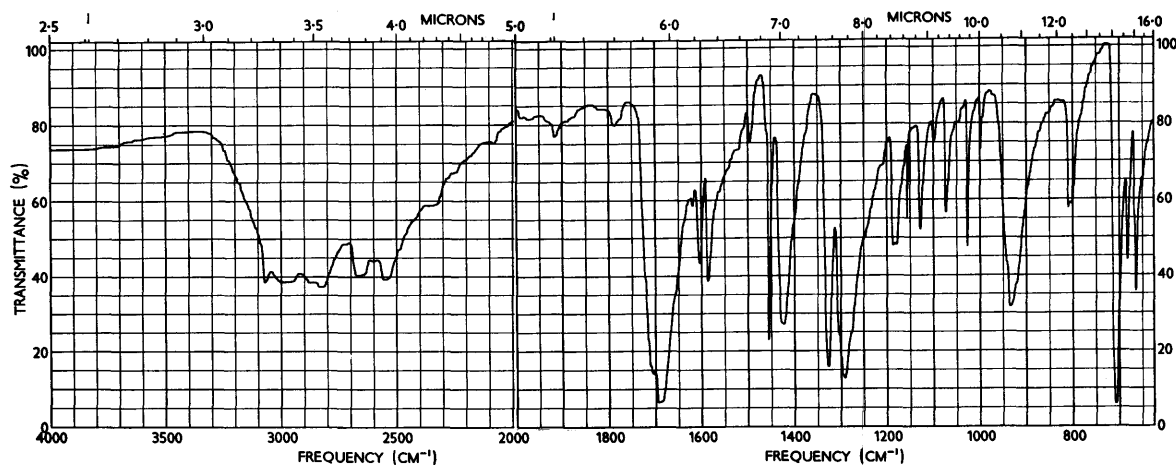
The broad absorption in the range 3300 to 2200cm^{-1}, with minor peaks, is very characteristic of carboxylic acid dimers. The carbonyl stretching frequency, $\nu_{C=O}$, of such dimers occurs near 1700cm^{-1}. Aromatic skeletal vibrations appear at 1600cm^{-1}. The band centred around 1300cm^{-1} is the ν_{C-O}. The molecular formula suggests that the compound is BENZOIC ACID.
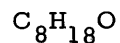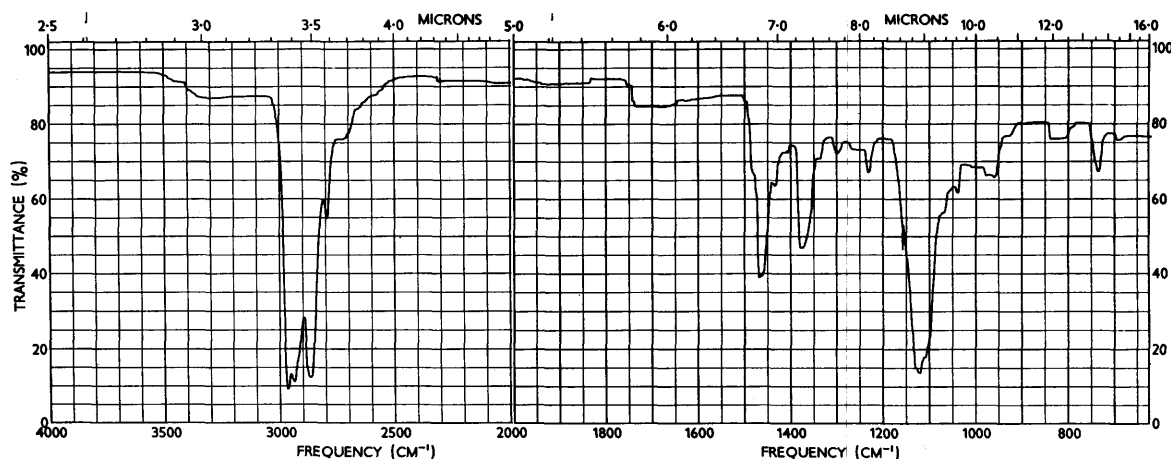
There is no indication of olefins or aromatic compounds since in the ν_{CH} region all the bands lie below 3000cm^{-1}. The spectrum is largely featureless; it shows the typical alkyl deformations at 1460 and 1375cm^{-1}. However, the appearance of a band at 720cm^{-1} (CH$_2$ rocking mode) would suggest a chain of four carbon atoms, i.e. an n-butyl group. The only dominant band of the spectrum is at 1130cm^{-1}. Its intensity and breadth suggest the C-O-C stretch of a symmetrical saturated ether. The compound is DI-n-BUTYL ETHER.
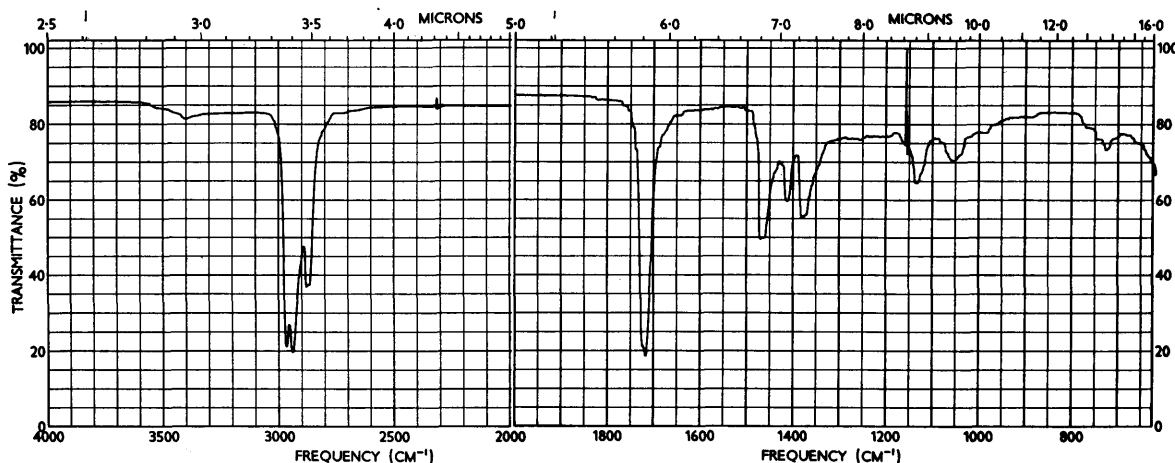
Absorption below 3000cm^{-1} indicates alkyl groups. No aromatic or olefins. The sharp intense band at 1720cm^{-1} is due to a carbonyl grouping. It could be a ketone, aldehyde or ester. The absence of a ν_{C-O} rules out an ester. The aldehyde possibility is also ruled out by the absence of the two very characteristic ν_{CH} frequencies at 2700 and 2800cm^{-1}. Our compound is therefore a ketone. This substance is n-BUTYL n-HEXYL KETONE.
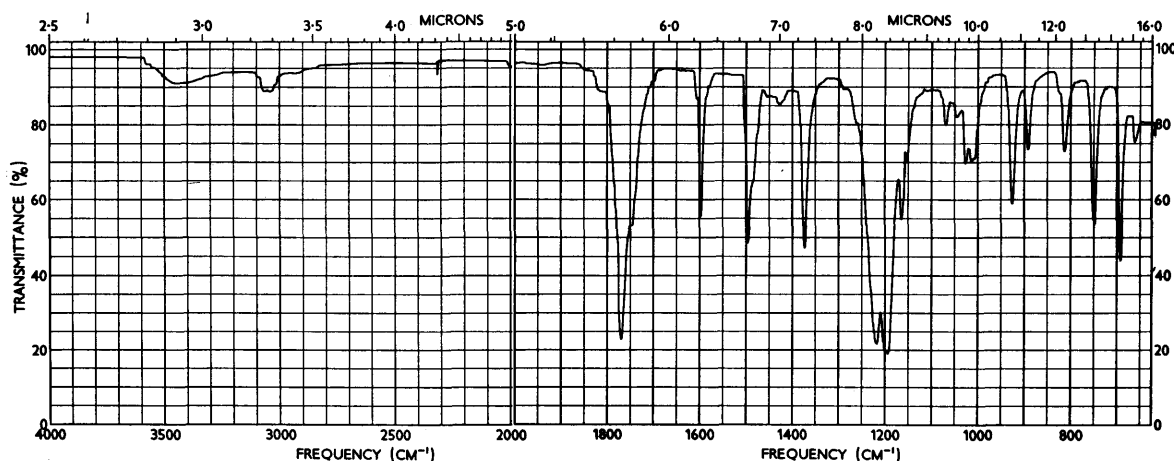
Absorption above 3000cm^{-1} indicates unsaturation. Aromatic skeletal vibrations appear at 1600 and 1500cm^{-1}. The carbonyl frequency, $\nu_{C=O}$, at 1770cm^{-1} strongly suggests an ester. This is confirmed by the ν_{C-O} at 1200cm^{-1}. The substitution pattern of the γ_{CH} leads us to a monosubstituted benzene ring. The intensity of the 1375cm^{-1} band is worthy of note. Rarely is the CH$_3$ deformation (sym.) so intense unless the CH$_3$ group is attached to a carbonyl grouping. The molecular formula suggests the compound is PHENYL ACETATE.
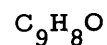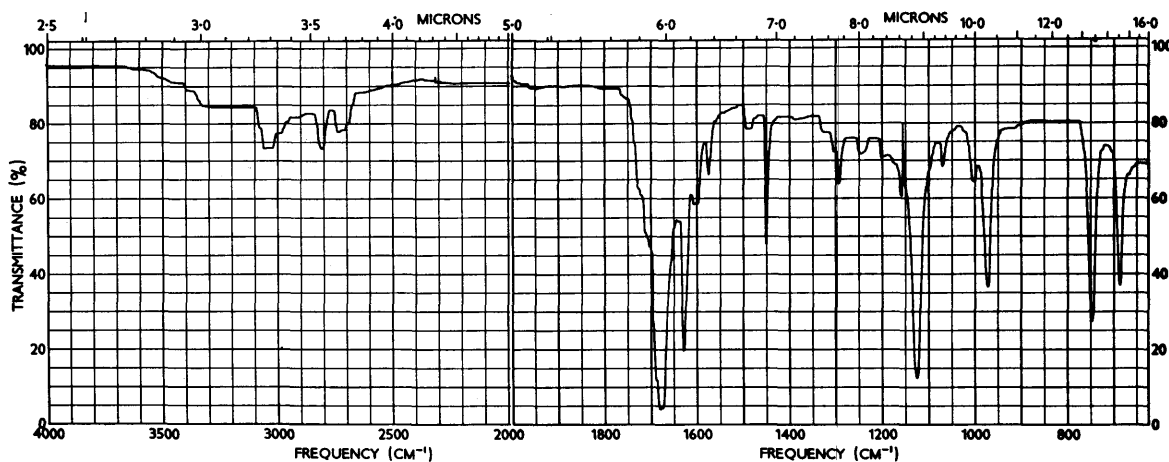
Absorption above $3000cm^{-1}$ indicates unsaturation. The two ν_{CH} absorptions at 2700 and $2800cm^{-1}$ indicate an aldehyde. The strong carbonyl absorption at $1690cm^{-1}$ supports this view. The low value for the $\nu_{C=O}$ could be explained by conjugation. Aromatic skeletal vibrations appear at 1600 and $1500\ cm^{-1}$. In addition, there is a $\nu_{C=C}$ at $1635cm^{-1}$. The absorbtion band at $990cm^{-1}$ (γ_{CH}) supports a trans double bond. By inspection of the 600 to $800cm^{-1}$ region the benzene ring is monosubstituted. The molecular formula leads us to CINNAMIC ALDEHYDE.
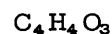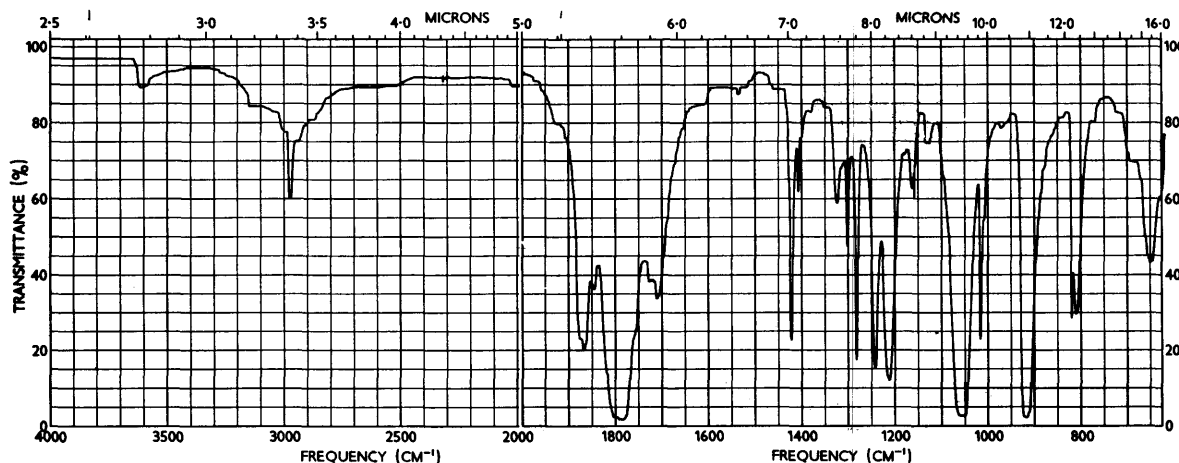
Absorption below $3000cm^{-1}$ suggests alkyl groups. The high frequency and complex nature of the $\nu_{C=O}$ at $1800cm^{-1}$ strongly favours a cyclic anhydride. The absence of any CH_3 groups is noted by the lack of absorption near $1460cm^{-1}$. However, the presence of a strong deformation frequency at $1420cm^{-1}$ supports CH_2 groups adjacent to carbonyl groups. This substance is SUCCINIC ANHYDRIDE.

Introduction

Nuclei with odd values of either mass or atomic number have magnetic moments and can be studied by the NMR technique, but the organic chemist is interested in this method chiefly because of the existence of the "chemical shift". This term refers to a screening effect that acts on a nucleus in a magnetic field. It is produced by the induced diamagnetic circulation of the valency electrons, and it is called a "chemical shift" because of the way in which its magnitude depends upon the state of chemical combination of the nucleus. The study of the NMR spectrum can therefore provide valuable information about the structural relationships.

Of the elements most commonly encountered in organic chemistry, ^{12}C and ^{16}O are not magnetic and their only contribution to the results is the effect they have on the environment of other nuclei. This means that the very large number of organic molecules containing just H, C and O atoms give a spectrum due to protons only, free from complications due to the spins of the other nuclei (apart from the small effects of the minute concentration of ^{13}C and ^{17}O, which do possess a magnetic moment). The phenomenon of NMR therefore presents an aspect of the molecule ripe for study. ^{1}H, ^{19}F, ^{31}P and ^{11}B are the magnetic nuclei which have excited the most interest. Halogens apart from fluorine normally exhibit no resonance signals, nor do they have any direct effect on the hydrogen resonances - except in so far as their electron affinity influences the environment of neighbouring nuclei and changes the screening effect.

The symbol for the nuclear magnetic moment is μ, and when nuclei which possess a dipole are placed in a magnetic field H_0 they will precess about the H_0 vector with a frequency v which is directly proportional to the field strength and dependent upon the value of μ, the magnetic moment characteristic of the type of nucleus. The classification of the nucleus is completed by knowledge of its spin quantum number (I). At this point it is worthwhile to quote the general principles of quantum mechanics, which state that the maximum measurable component of the angular momentum of a nucleus must be an integral or half integral multiple of $h/2\pi$ (where h is Planck's constant). This maximum component is then written as I, the spin quantum number.

These symbols are related in an equation that defines the basis of NMR experimentation, i.e. to induce transition with the emission or absorption of energy quanta, between any of $2I+1$ orientations open to a nucleus in a static field H_0. Then, for a transition between neighbouring levels,

$$v = \frac{\mu H_0}{\hbar I}$$

so that v is 60 Mc/s for an H_0 of approximately 14,000 gauss.

The results obtained in practice illustrate how similar protons in different environments are more or less affected by the "chemical shift" – the screening effect in a magnetic field. Very few protons are shielded more than those in tetramethylsilane, which therefore absorbs at highest applied magnetic field. It has been found useful to include a trace of this with the sample as an internal standard, whereupon, by comparison, the chemical shift of other protons in the sample may be calculated from the expression

$$\delta = \frac{(H_r - H_s)}{H_r}$$

where H is the field experienced by the reference and H_s that experienced by the sample. Since the field strength is proportional to the frequency,

$$\delta = \frac{(\text{frequency diff.}) \times 10^6}{\text{frequency of the oscillator}}$$

where the frequency difference between sample and reference is negative if the sample line is at a lower frequency than the reference line (the factor 10^6 is included to give convenient numbers for proton spectra in order that δ shall be expressed in ppm). From this and Tiers convention we have:

$$\tau = 10 - \delta$$

$$= 10 - \frac{(\text{frequency diff. from SiMe}_4) \times 10^6}{\text{osc. frequency (c/s)}}$$
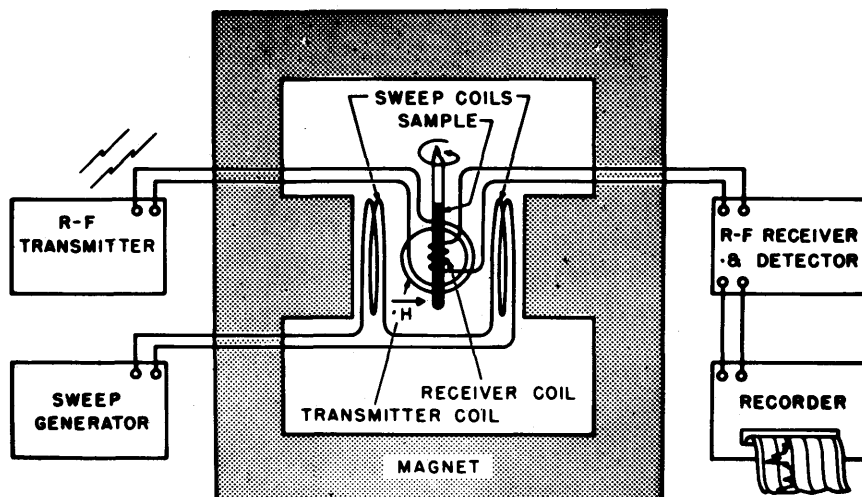
Schematic diagram of an NMR Spectrometer

The coupling constant is a measure of electron coupled magnetic interaction between neighbouring nuclei. Apart from the chemical shift considerations already mentioned, the field experienced by nuclei of one group, protons for example, is influenced by the spins of protons in the neighbouring group. In this instance, a neighbouring proton can take up one of two orientations in a magnetic field, parallel or anti-parallel to the main vector. Thus, in the case of the resonance of the one single proton in acetaldehyde, this proton is interacting with the three protons in the methyl group of acetaldehyde, and eight different possible arrangements suggest themselves. Either all three protons, or two of them (there are three versions of this all effectively equivalent) can be aligned parallel to the main vector or they can equally well take up anti-parallel positions. This means that the resonance of the single proton is split by spin-spin interaction with the other three protons. The result is a quartet whose band intensities are in the ratio 1:3:3:1. Thus multiplet spacing can confuse the spectra unless the chemical shift between the interacting groups is large enough to afford complete separation. The separation of adjacent components in a multiplet will be equal to each other and to the separation of the components in the multiplet arising from the second group involved in mutual splitting. This separation is a direct measure of the electron coupled spin-spin interaction and is known as the coupling constant J. J is independent of the field strength when measured in cycles/sec.
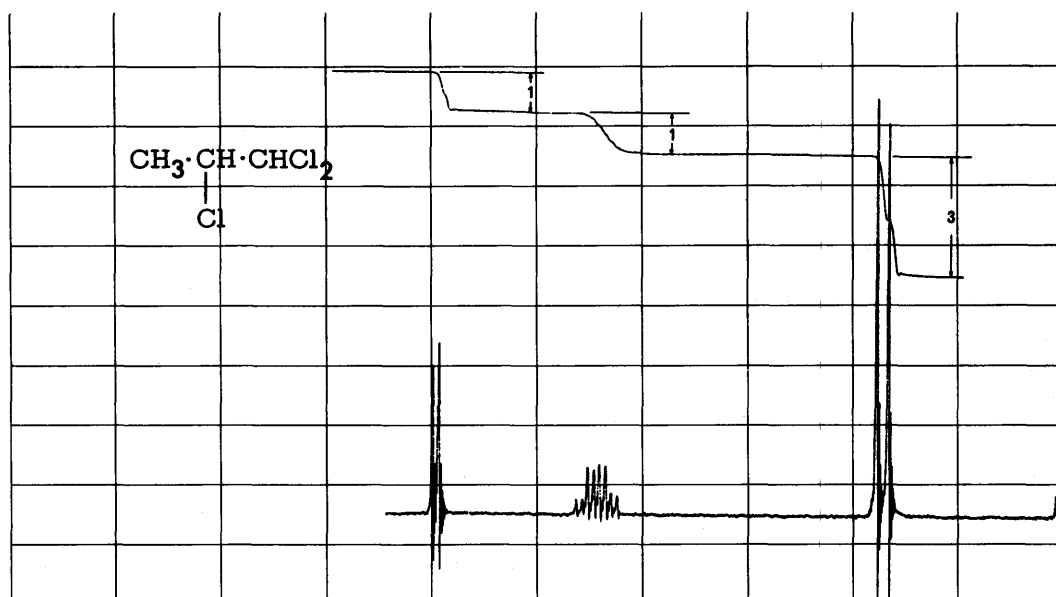
Proton Magnetic Resonance Spectrum of 1:1:2-Trichloropropane

Coupling between widely separated groups in a molecule is unusual and it is normally safe to assume that spectral evidence of coupling indicates close proximity between the participating groups. When the coupling constant J is of the same order as the chemical shift, complicated spectra are likely to result, and the multiplicity rules will be broken. If, however, the sample under examination were to be specially irradiated at the resonance frequency of one participant in a spin-spin interaction, the interaction of the coupled neighbour is averaged to zero, with the net result that the band appears as a single one. Thus the spectrum is simplified and the interacting groups identified from their chemical shift.

The method can be used to show the chemical shift of groups which are completely hidden by unrelated resonances.

The simplest double resonance apparatus employs two R.F. frequencies at a known separation with normal field sweep. The separation is made equal to the separation between the group to be decoupled and the group to be observed. This is known as the field sweep technique. It works well for simple spectra in which the groups are well separated.

To observe an extensive spectrum while saturating a particular group, frequency sweep is essential. The region under observation is swept repeatedly while the saturating frequency is changed after each sweep by means of the field shift controls. The Perkin-Elmer accessory provides for both field and frequency sweep operation.
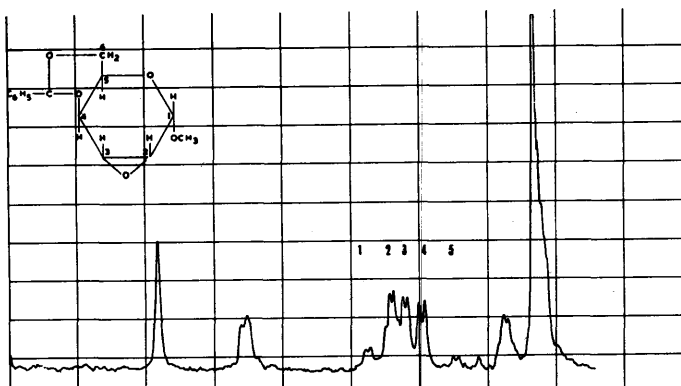
(a) The resonance spectrum of methyl-2:3-anhydro-4:6-benzylidene-O-d-glucoside.
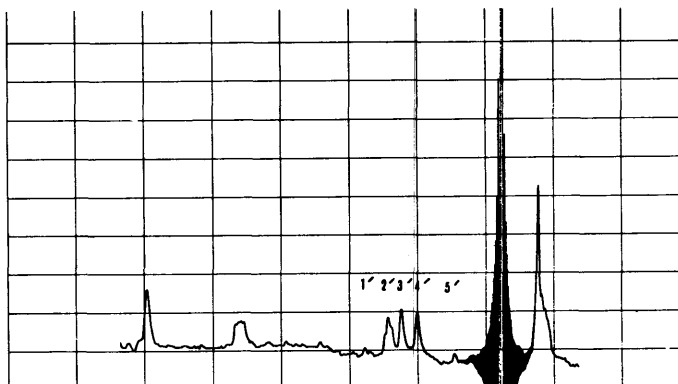
(b) The same spectrum under double resonance conditions, using the frequency sweep technique.

In the chain of CH groups on the 6-membered ring each proton couples with its neighbours. When the coupling produced by individual protons is removed by means of double irradiation, resonances of adjacent protons become simplified.   By irradiating each resonance in turn the sequence of protons in the molecule can be related to the resonances observed. The heavy beat in the lower figure indicates the position of the decoupling energy which has simplified the multiplets 1 to 5. The new lines 1'3'4'5' can be recognised as an AB spectrum, and the group 2 is changed from a quartet to a triplet.   The only proton which could produce such a change is that on C_5. The AB spectrum is from the methylene and the group 2 is from the proton at C_4. Further experiments give an unambiguous assignment for the remaining resonances.
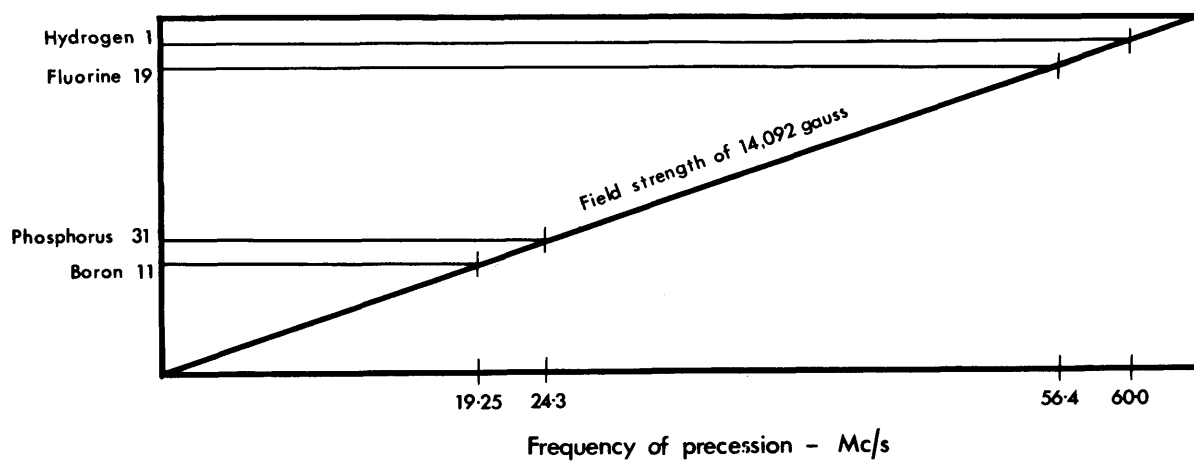
Operational Frequencies of Some Magnetic Nuclei

PROTONS

In this routine proton spectrum, the example given is hecogenin acetate, a steroid intermediate.
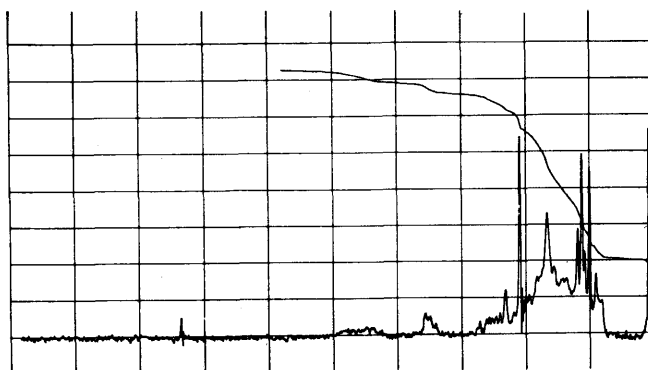
FLUORINE

This fluorine spectrum has been obtained with the same bridge and probe as used for protons after simply switching a plug on to the separate R.F. amplifier source provided for fluorine. In this case $CH_2:CH.SF_5$ has been examined as a pure liquid. The complete AB_4 spectrum is not shown. We illustrate the A part; the resonance due to a single nucleus split into $(2nI + 1)$ (9) lines. Four equivalent fluorine nuclei are coupled to a non-equivalent fifth.
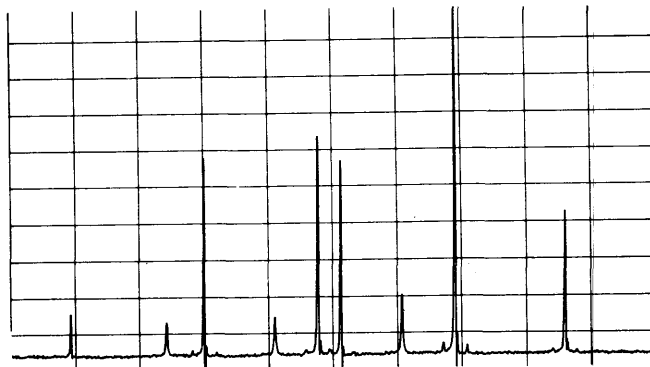
BORON

Boron spectra can also be obtained within a few minutes of spectra being run on other nuclei. A plug-in R.F. amplifier source is available and the appropriate bridge control is substituted over the probe which accepts the 8·5mm unspun tube. Here we show the spectrum of $NaBH_4$. The four protons split the boron resonance into five bands.
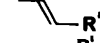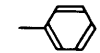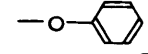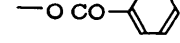
PHOSPHORUS

Phosphorus work has its own R.F. amplifier source and bridge controls, but the probe is the same as for boron, accepting 8·5mm unspun tubes. The changeover takes a matter of a few minutes. This sample of commercial triphenyl phosphite is contaminated. The band on the left due to the pure compound is joined by the two bands of diphenyl phosphite and the band on the right which is attributed to triphenyl phosphate.
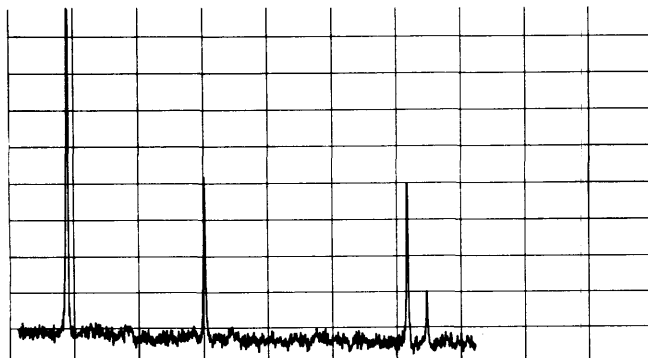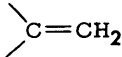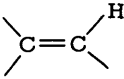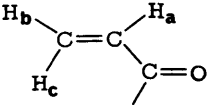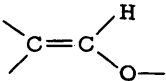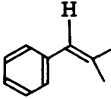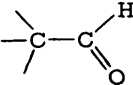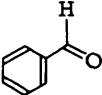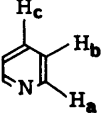
Approximate Tau Values for the Protons of Methyl, Methylene, and Methine Attached to Various Groups R

(R' and R" represent hydrocarbon residues)

R	$CH_3 \cdot R$	$R" \cdot CH_2 \cdot R$	$R" \cdot CH \cdot R$
$-\overset{.}{\underset{.}{C}}\cdot$	9·10	8·75	8·50
(vinyl)	8·30	8·10	
(vinyl)—R'	8·10		
(vinyl)—R'	8·00		
$-CO_2R'$	8·00	7·90	
$-CN$	8·00		
$-CO_2H$	7·93	7·66	7·43
$-CONR'_2$	7·98	7·95	
$-COR'$	7·90	7·60	7·52
$-CHO$	7·83	7·80	7·61
(cyclopropyl) R'	7·90		
$-SR'$	7·90	7·60	
$-NR'_2$	7·85	7·50	7·13
$-I$	7·85	6·85	5·80
(phenyl)	7·66	7·38	7·13
$-NH\cdot COR'$	7·15	6·80	
$-Br$	7·30	6·70	5·90
$-Cl$	6·95	6·60	6·00
$-OR'$	6·70	6·65	6·20
$-OH$	6·62	6·44	6·15
$-O\cdot COR'$	6·35	5·85	4·99
$-O-$(phenyl)	6·30	6·10	
$-O\,CO-$(phenyl)	6·10	5·77	4·88

Approximate Tau Values For Protons on Unsaturated Groups

Structure	Tau Value
$-C\equiv CH$	7·65
$>C=CH_2$	5·35
$>C=C<^H$	acyclic 4·60 cyclic 4·40
H_b, H_a, H_c (enone)	H_a 4·20 H_b 4·00 H_c 3·80
$>C=C<^H_{O-}$	3·20
(phenyl-propenyl)	3·00
(benzene) -H	2·73
$>C-C<^H_O$	0·35
(benzaldehyde)	0·10
(pyridine) H_c, H_b, H_a	H_a 1·50 H_b 3·01 H_c 2·65

Shoolery's Rules

CH_4	9·84 Tau

Subtract for each substituent:

—CH_3, alkyl	0·47

$$\underset{\diagdown}{R^1}\diagup C = C \diagup\underset{R^3}{\overset{R^2}{\diagdown}}$$

	1·32
—C≡CH	1·44
—NR^1R^2	1·57
—SR	1·64

$$\underset{R}{\overset{\diagdown}{\diagup}} C = O$$
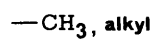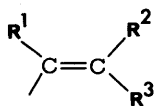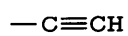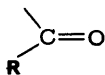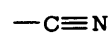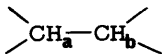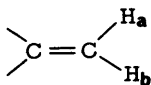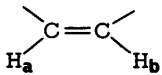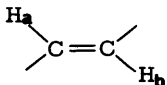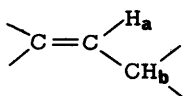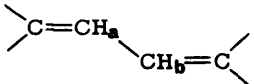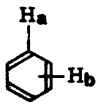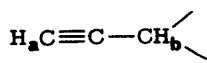
	1·70
—C≡N	1·70
—I	1·82
—⬡	1·83
—Br	2·33
—O	2·36
—Cl	2·53

Proton Proton Spin Coupling Constants

J_{ab}

$\begin{array}{c} \diagdown \\ \diagup \end{array} C \begin{array}{c} H_a \\ H_b \end{array}$ 8 - 20 cps depending on $H\hat{C}H$

$\diagdown CH_a{-}CH_b \diagup$ 0 - 12 cps depending on dihedral angle

$\diagdown C = C \begin{array}{c} H_a \\ H_b \end{array}$ 0 - 3·5

$\begin{array}{c} \diagup \\ H_a \end{array} C = C \begin{array}{c} \diagup \\ H_b \end{array}$ 5 - 14

$\begin{array}{c} H_a \\ \diagdown \end{array} C = C \begin{array}{c} \diagup \\ H_b \end{array}$ 11 - 19

$\diagdown C = C \begin{array}{c} H_a \\ CH_b \end{array}$ 4 - 10

$\diagdown C = CH_a{-}CH_b = C \diagup$ 10 - 13

ortho	7 - 10
meta	2 - 3
para	< 1

$H_aC \equiv C{-}CH_b \diagdown$ 2 - 3

Interpretation of Proton Magnetic Resonance Spectra

The simple rule to predict the number of lines or signals resulting from a coupling is to apply general formula (n + 1) where n is the number of equivalent neighbouring nuclei. When the multiplet results from equivalent nuclei, relative intensities are given by the coefficients in the development of $(r + 1)^n$, i.e.

<div align="center">

1:1

1:2:1

1:3:3:1

1:4:6:4:1

</div>

The coupled nuclei are denoted by letters of the alphabet A, B, C, ...M, N, ...X, Y, etc. When the chemical shift between nuclei is large compared with the coupling constant, then letters far apart are employed, e.g. AM, AX. When nuclei are similarly shielded, i.e. when the chemical shift between them is small and thus of the same order or less than the coupling constant, then letters close to one another in the alphabet are chosen, e.g. AB, ABC, AB_2. The subscript number as in B_2 denotes two identical coupled nuclei.

Strictly speaking, letters near the beginning of the alphabet should be reserved for the nuclei responsible for the lower field lines, in any given system, but this convention is by no means rigorously employed.

The following set of spectra are discussed in terms of some of these coupled systems. The convention used to denote chemical shift in this series of spectra is ppm (δ). The relationship between tau values and ppm is given by

$$\tau = 10 - \delta$$

The spectrum of 1,1,2-trichloroethane illustrates a typical AX_2 system, both the methine and methylene protons having vastly different chemical shifts. Thus the A proton is split into a triplet by the neighbouring equivalent methylene protons ($n=2$, hence $n + 1 = 3$) with intensity ratio 1:2:1. The two methylene protons, X_2, are in turn split into an equal intensity doublet ($n=1$). Integration of the area under each group of signals affords information on how many protons are represented by a particular group of signals i.e. 1H at 5·75 and 2H at 3·95 ppm. Finally the coupling constant J_{AX} is given by the distance between the two lines of the methylene signal and is also present in the triplet. The effect of chlorine nuclei is to deshield the proton and hence both signals are at lower field than those observed for similar groups with hydrocarbon substituents.
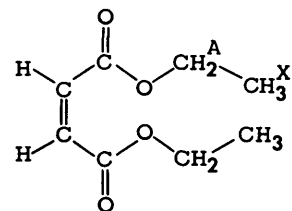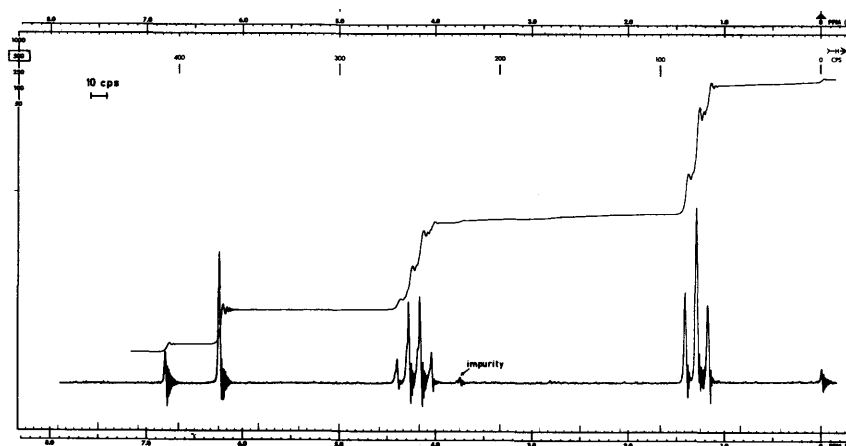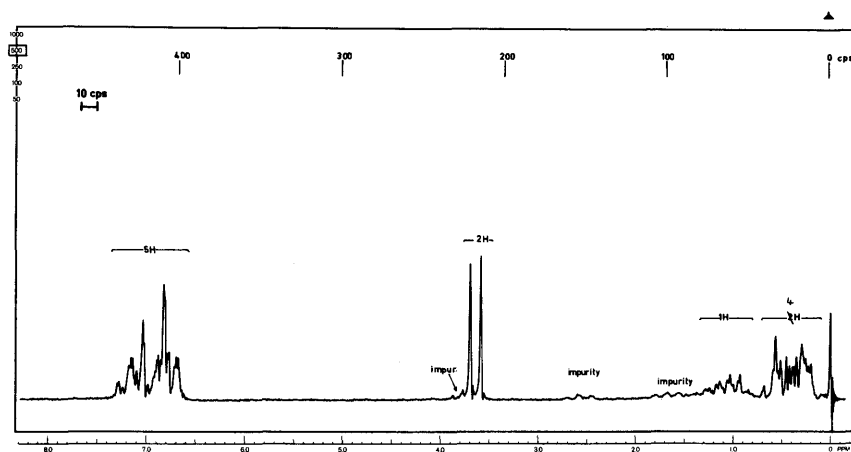
The spectrum of diethyl maleate illustrates an A_2X_3 system. The two equivalent methylene protons, A_2, are split to give a quartet (1:3:3:1) and the three equivalent methyl protons, X_3, a triplet (1:2:1). Furthermore one can conclude with some certainty that the grouping is present as $-O-CH_2CH_3$ since the methylene protons are removed to lower field (4·2δ) by being adjacent to an oxygen atom. The two olefinic protons are represented by a single signal at 6·2δ, i.e. they are chemically equivalent. The peak at 6·8δ is due to the chemically equivalent trans olefinic protons of the isomeric diethyl fumarate.

The first important point to notice about this spectrum is the presence of signals at very high field (0·2 to 1·2δ). These are very characteristic of cyclopropane protons. Integration tells us we have five protons of this class, one of which is at slightly lower field than the other four, i.e. the site of substitution. A methylene signal split into an equal intensity doublet appears at 3·65δ. The chemical shift value informs us that it is very probably adjacent to an oxygen atom. The fact that it is split into a doublet might suggest that it is also connected to the cyclopropyl ring. At about 6·9δ a group of signals representing five protons points to a mono-substituted benzene ring system. Taking into consideration all this information our compound is cyclopropylmethyl phenyl ether.
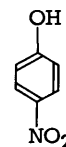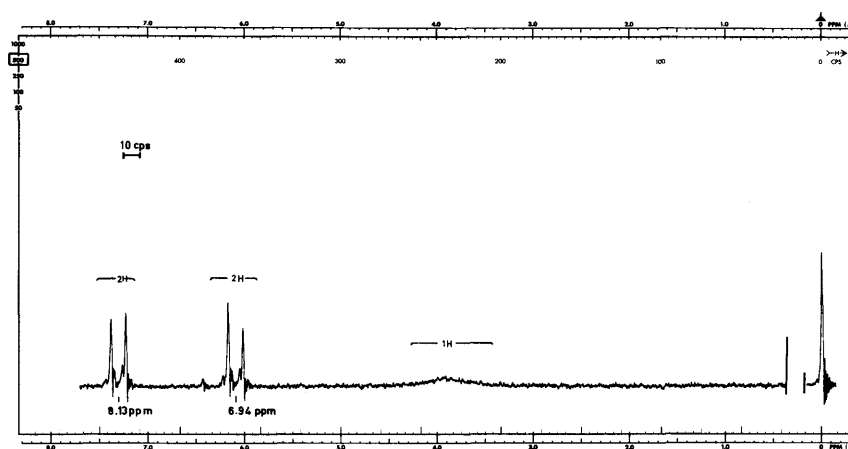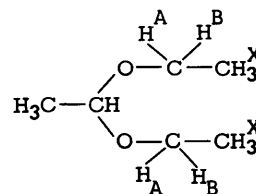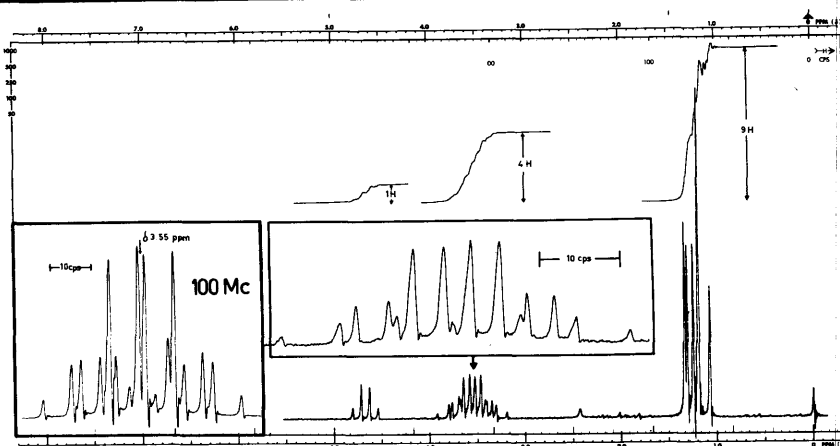
The spectrum of p-nitrophenol is a very good example of an A_2B_2 system. The protons ortho to the hydroxyl group having the same chemical shift couple with the protons ortho to the nitro group. The result is a 4 line spectrum with the intensity of the inner lines greater than the outer. In general, as the two chemical shift values approach close to one another the two inner lines gain in intensity at the expense of the outer until the two chemical shift values are one when we have a single line. On the other hand, as the chemical shift values move away from each other the lines gradually assume equal intensity i.e. from AB to AX.

The spectrum of acetaldehyde diethylacetal illustrates an ABX_3 system. In this particular case the two protons of the methylene group are not chemically equivalent. These constitute the AB part while the methyl protons are X_3.

Considering the AB part of the spectrum coupling between the A and B protons would give four lines, each of which would then be further split into quartets by the three equivalent methyl protons (X_3), i.e. AB spectrum would consist of 16 lines. Under the very high resolution of the 100 Mc instrument we find that we do in fact have 16 lines recorded. It is conceivable that some lines may overlap in other less straightforward cases, i.e. the number of lines observed will be less than the maximum 16.
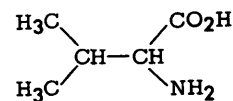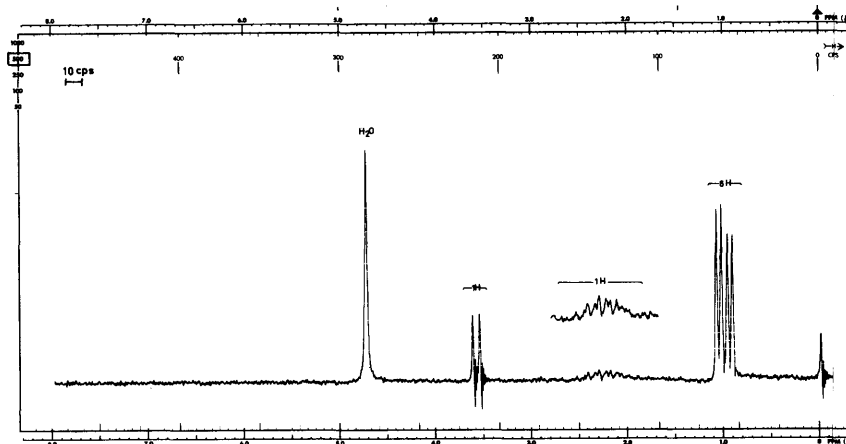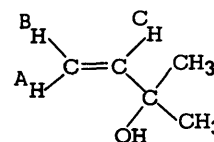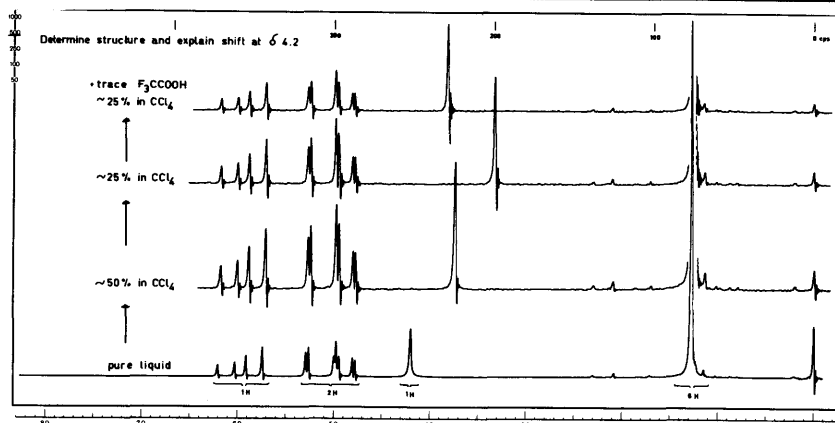
This spectrum is yet another example of two similar groups of protons having different chemical shifts. In this case the two methyl groups differ slightly in chemical shift value (0·95 and 1·16) and are both split into equal intensity doublets by the adjacent methine proton at 2·26 which in turn is split into a 7 line spectrum, and finally into a 14 line spectrum by the methine proton on the same carbon carrying the amino and carboxyl groups. The absence of both the OH and NH_2 protons is easily explained as they have exchanged in heavy water to the deutero derivatives.

The spectrum of 2-methylbut-3-en-1-ol illustrates two very interesting points. The first is that the vinyl protons represent an ABC system. This is one of the more complex spin-coupling systems and sets of calculated spectra (i.e. changing values of coupling constants and signs) are given by WIBERG and NIST (Interpretation of NMR Spectra, Benjamin, 1962). A search through these to find one which matches the recorded pattern often saves time and calculation.

The second interesting feature of the spectrum is that the signal at 4·2δ (pure liquid) changes its chemical shift value depending on the sample preparation. This signal is due to the hydroxylic proton and results from the ability to proton transfer with neighbouring molecules. The signal we are observing is the mean of the two extreme positions during the exchange cycle. As we dilute the solution the signal progressively moves upfield. The chemical shift range for alcohols is from 5·5 to 0·7δ, the upper limit representing extrapolation to infinite dilution.
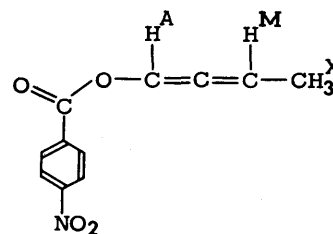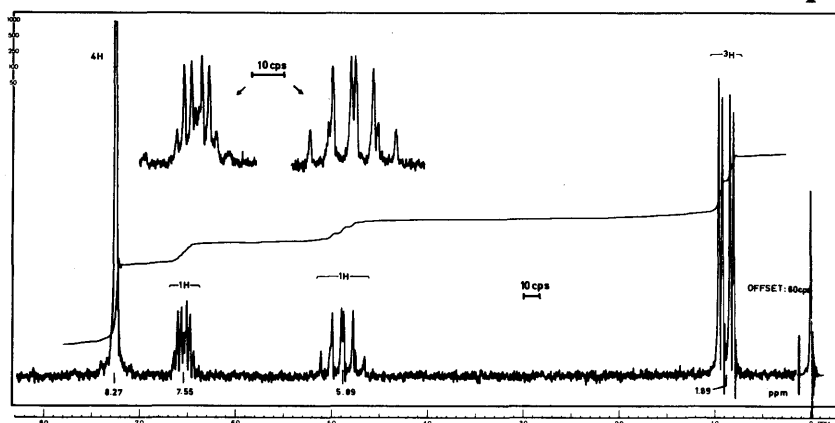
The allene system represents one of the few cases where coupling through four and five bonds is observed (normally coupling is limited to through three bonds). The two allene protons (A and M) and the three methyl protons (X_3) represent an AMX_3 system. The methyl protons are first split by the adjacent M proton into two lines (large coupling constant) and then further split by the A proton (but with a much smaller coupling constant) into 4 lines. Both the A and M protons signals are 8 line spectra.

Introduction

The mass spectrometer is a sensitive instrument which is able to sort and identify atoms or molecules of various masses by means of a magnetic field. The particles are ionized (i.e. given an electric charge) and are then directed across a magnetic field which bends their flights into circular paths. The heavier of two ions will fly in a wider arc than the lighter one and hence hit a different target.

Basically the instrument records the decomposition of a molecule resulting from electron bombardment as positive ion fragments separated on the basis of mass (strictly speaking, mass/charge, but in practice most ions are singly charged.) This mode of separation of a mixed stream of ions by mass can be considered analogous to the separation of a beam of white light by a glass prism into a spectrum of its constituent component colours or wavelengths of light.
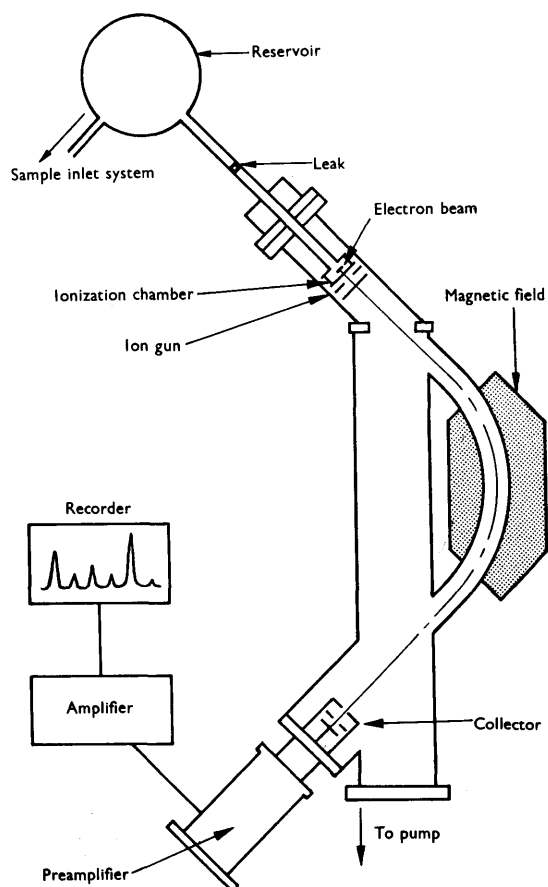
A molecular ion (called the parent ion) is formed by interaction with the beam electrons (removal of a single electron) at an energy of about 10 to 15 electron volts. The recognition of this parent ion is of great importance as it gives the organic chemist the exact numerical molecular weight. Mass spectra, however, are usually obtained at electron beam energies of about 70 electron volts and the resultant spectrum records the breakdown pattern. Such a presentation of the masses of the resulting fragment ions against their relative abundances constitutes the mass spectrum of the compound. The largest peak in the spectrum, called the "base" peak, is assigned a value of 100%, and the remaining peaks are reported as percentages of the base peak.

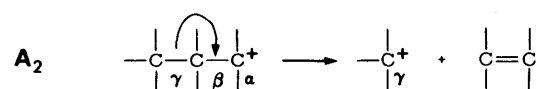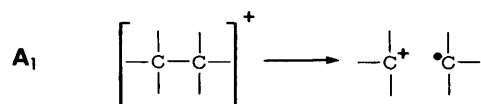← Schematic Diagram of the MS 2 Mass Spectrometer

- 53 -
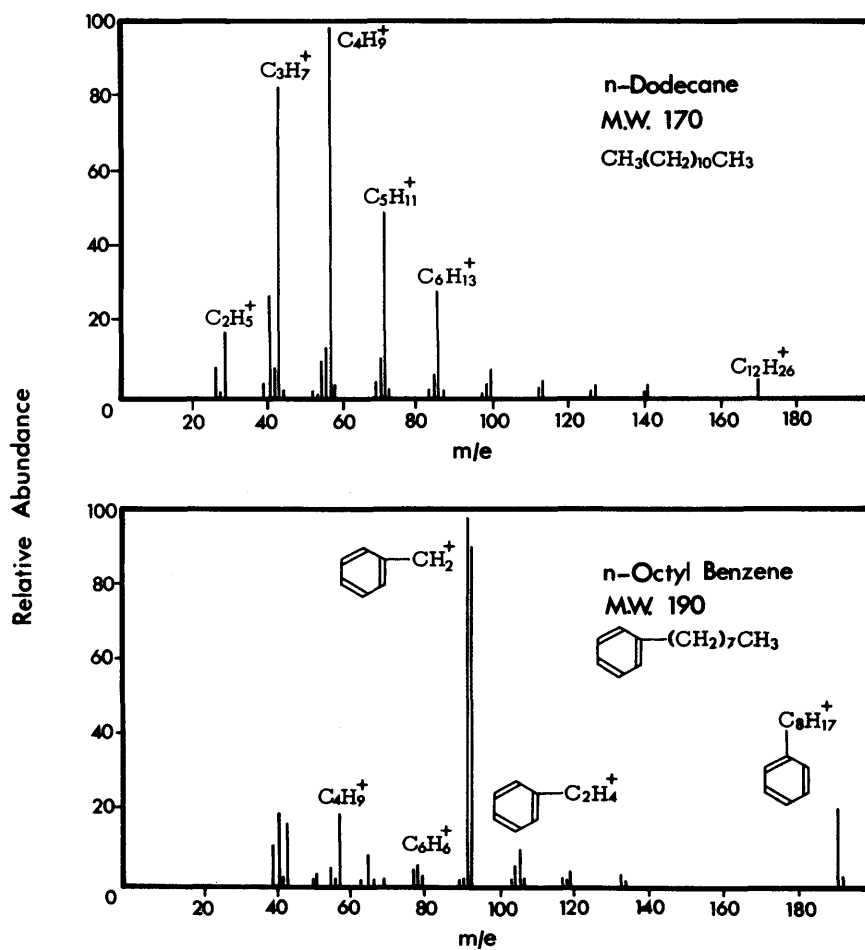
The extremely low vapour pressure (10^{-5}) within the mass spectrometer allows us to consider that breakdowns occur via unimolecular decompositions. On the basis of the concepts of statistics, resonance, hyperconjugation, polarizability, and inductive and steric effects, a set of general rules can be formulated to predict prominent peaks in the spectrum. BIEMANN (Mass Spectrometry, p. 76-77) has summarised these fragmentation processes as follows:-
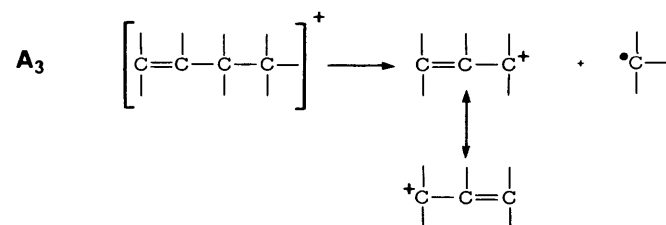
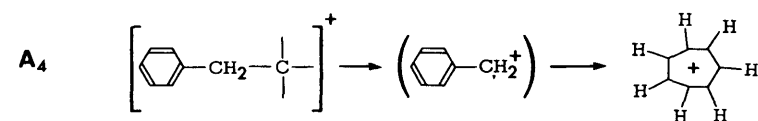## Summary of Fragmentation Processes

Simple cleavage:

Fission of carbon-carbon bonds in saturated hydrocarbons. Order of ability to stabilize positive charge on a carbonium ion is tertiary >secondary >primary. This results in preferred cleavage at branched carbon atoms. When a choice is possible the largest substituent is lost in this cleavage.

A₁

$$\left[-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \right]^{+} \longrightarrow -\overset{|}{\underset{|}{C}}{}^{+} + {}^{\bullet}\overset{|}{\underset{|}{C}}- $$

A₂

$$-\overset{|}{\underset{|\,\gamma}{C}}-\overset{|}{\underset{|\,\beta}{C}}-\overset{|}{\underset{|\,\alpha}{C}}{}^{+} \longrightarrow -\overset{|}{\underset{|\,\gamma}{C}}{}^{+} + \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}$$
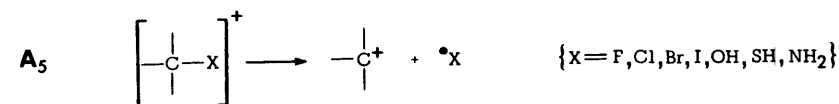
Allylic cleavage resulting in resonance stabilized carbonium ion. Especially prominent in molecules where the double bond cannot easily migrate or is located near another functional group.
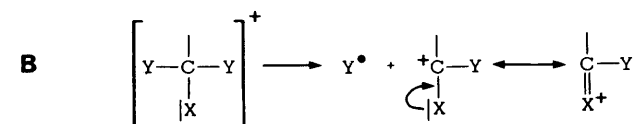
A₃

$$\left[\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \right]^{+} \longrightarrow \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}{}^{+} + {}^{\bullet}\overset{|}{\underset{|}{C}}-$$

$$\updownarrow$$

$$ {}^{+}\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}$$

Benzylic cleavage of an aromatic ring side chain resulting in ion of mass 91. In general, this ion rearranges to the very stable tropyllium ion.
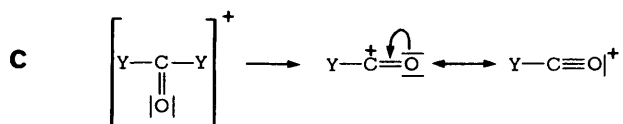
A₄

$$\left[\langle \bigcirc \rangle -CH_2-\overset{|}{\underset{|}{C}}- \right]^{+} \longrightarrow \left(\langle \bigcirc \rangle -CH_2^{+} \right) \longrightarrow \text{(tropyllium ion)}$$

Loss of radical by homolytic cleavage.

A₅

$$\left[-\overset{|}{\underset{|}{C}}-X \right]^{+} \longrightarrow -\overset{|}{\underset{|}{C}}{}^{+} + {}^{\bullet}X \qquad \{X = F, Cl, Br, I, OH, SH, NH_2\}$$

Cleavage α to carbonyl group.

B

$$\left[Y-\overset{|}{\underset{|X}{C}}-Y \right]^{+} \longrightarrow Y^{\bullet} + {}^{+}\overset{|}{\underset{|X}{C}}-Y \longleftrightarrow \overset{|}{\underset{X^{+}}{C}}-Y$$

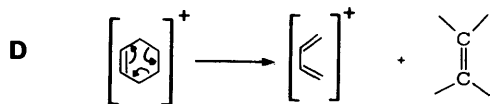**Fission α to carbon** substituted with heteroatom with lone pairs available to enter bonding and increase stability of resulting ion.

C

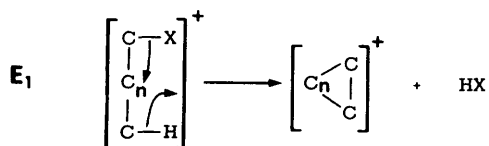$$\left[Y-\underset{\underset{|O|}{\|}}{C}-Y \right]^+ \longrightarrow Y-\overset{+}{C}=\underline{O} \longleftrightarrow Y-C\equiv O|^+$$

Retro-Diels-Alder process. Ring with suitably substituted double bond can break as shown provided it is energetically favoured.
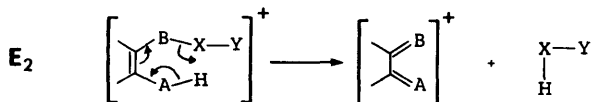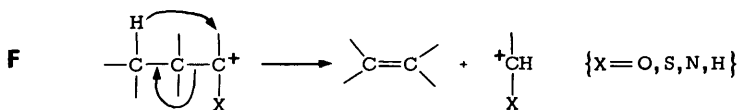
D

$$\left[\bigcirc \right]^+ \longrightarrow \left[\diagup\!\!\!\diagdown \right]^+ \; + \; \overset{\diagdown\;\diagup}{\underset{\diagup\;\diagdown}{\overset{C}{\underset{C}{\|}}}}$$

Rearrangements:

Elimination of neutral molecule involving rearrangement of one hydrogen atom to the elided fragment. A cyclic ion is left.
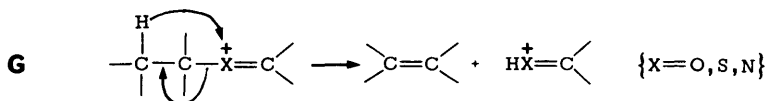
E₁

$$\left[\begin{matrix} C-X \\ | \\ C_n \\ | \\ C-H \end{matrix} \right]^+ \longrightarrow \left[C_n \overset{C}{\underset{C}{\diagup\;|\;\diagdown}} \right]^+ \; + \; HX$$

Elimination of neutral molecule by rearrangement involving cis double bond or aromatic double bond.

E₂

$$\left[\overset{B\; X-Y}{\underset{A-H}{\diagup\!\!\diagdown}} \right]^+ \longrightarrow \left[\overset{B}{\underset{A}{\diagup\!\!\diagdown}} \right]^+ \; + \; \underset{H}{\overset{X-Y}{|}}$$

Elimination of neutral molecule by rearrangement from ion produced by type B fission.

F

$$-\overset{H}{\underset{|}{C}}-\overset{|}{C}-\overset{|}{C}^+ \longrightarrow \overset{\diagdown}{\underset{\diagup}{C}}=\overset{\diagup}{\underset{\diagdown}{C}} \; + \; \overset{+}{\underset{X}{C}}H \quad \{X=O,S,N,H\}$$

Elimination of neutral molecule from resonance form of the type B.

G

$$-\overset{H}{\underset{|}{C}}-\overset{|}{C}-X=C \longrightarrow \overset{\diagdown}{\underset{\diagup}{C}}=C \; + \; H\overset{+}{X}=C \quad \{X=O,S,N\}$$

So called **McLafferty rearrangement**. Five centres plus one double bond and a transferable γ-hydrogen atom are required. Very widespread process in molecular decomposition.

H

$$\left[\begin{matrix} A \overset{H}{\frown} B \\ | \quad \| \\ Y\; X\; C \end{matrix} \right]^+ \longrightarrow \overset{A}{\underset{Y}{\|}} \; + \; \left[\begin{matrix} H \diagdown B \\ \quad | \\ X\!\!=\!\!C \end{matrix} \right]^+$$
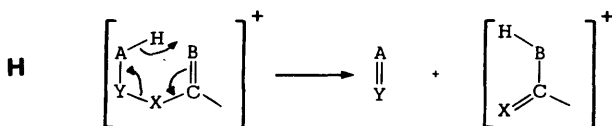
Interpretation of Mass Spectra

The following six mass spectra are explained in some detail and serve to illustrate a few of the fragmentation processes tabulated by BIEMANN.
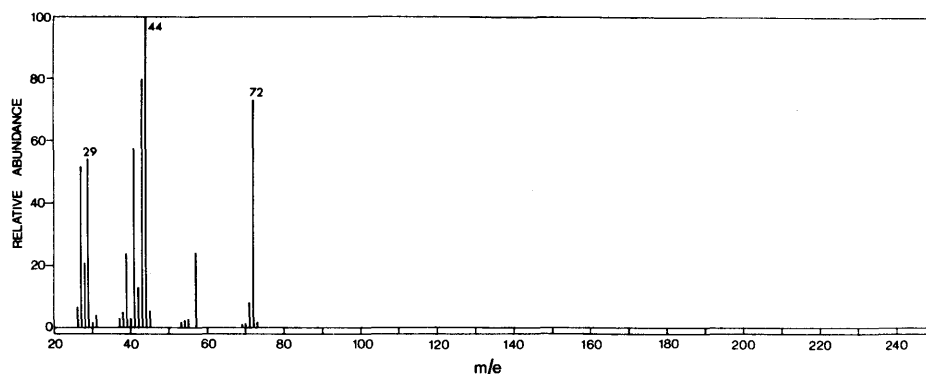
The base peak of the spectrum is at m/e 44 which must be a rearrangement peak since it occurs at an even mass number. This rearrangement peak results from transfer of a γ-hydrogen to the carbonyl oxygen with simultaneous β-fission via a six-membered cyclic transition state. The β-cleavage may also occur with hydrogen transfer but with the charge now residing on the alkyl fragment, i.e. M-44. Finally the β-cleavage can also occur without γ-hydrogen transfer, the charge remaining with the alkyl group, i.e. M-43.
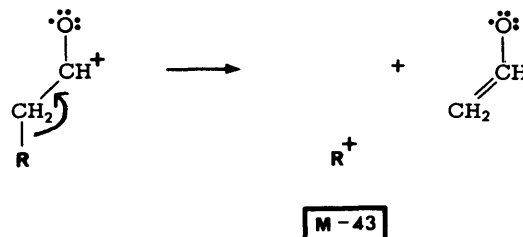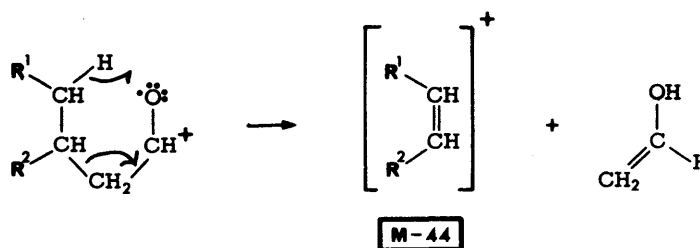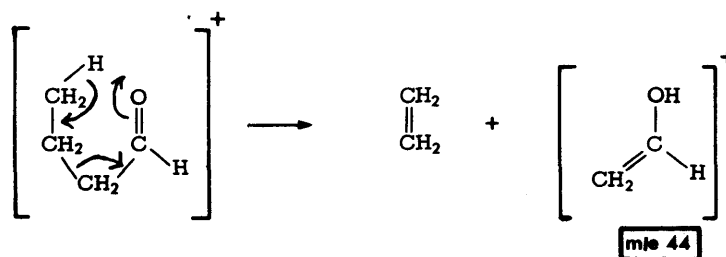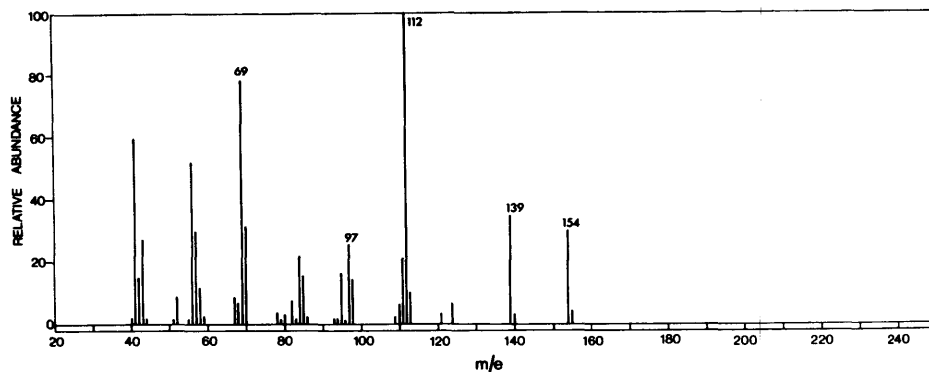
The base peak of the menthone spectrum is at m/e 114 i.e. a rearrangement peak.   As in the case of butyraldehyde this fragment results from transfer of a γ-hydrogen from the isopropyl group with simultaneous β-cleavage. If α-cleavage of the molecular ion occurs with the form-ation of a secondary radical, subsequent hydrogen transfer and γ-bond rupture yield m/e 69. This is the methyl homologue of the ion which is the base peak (m/e 55) in the spectrum of cyclohexanone.
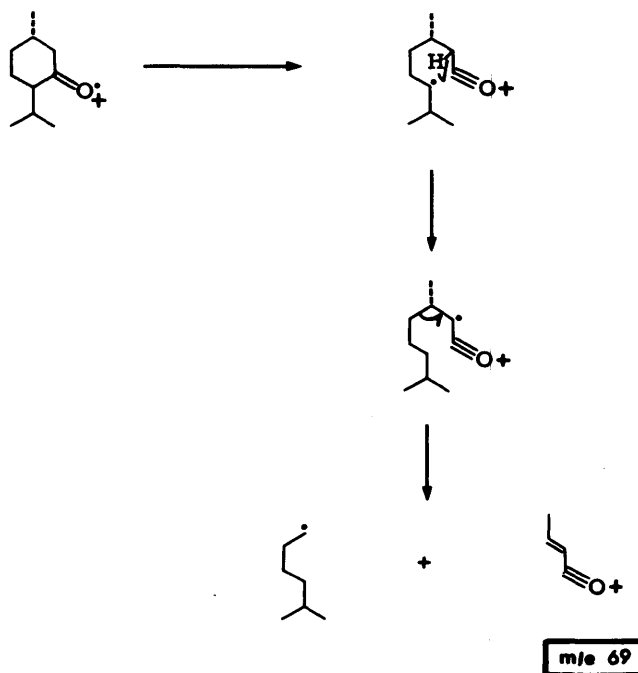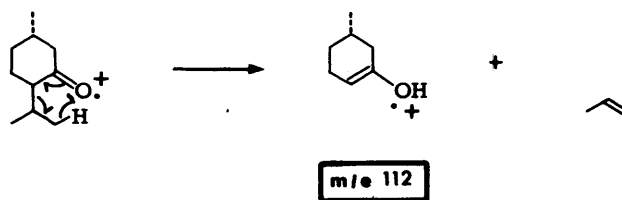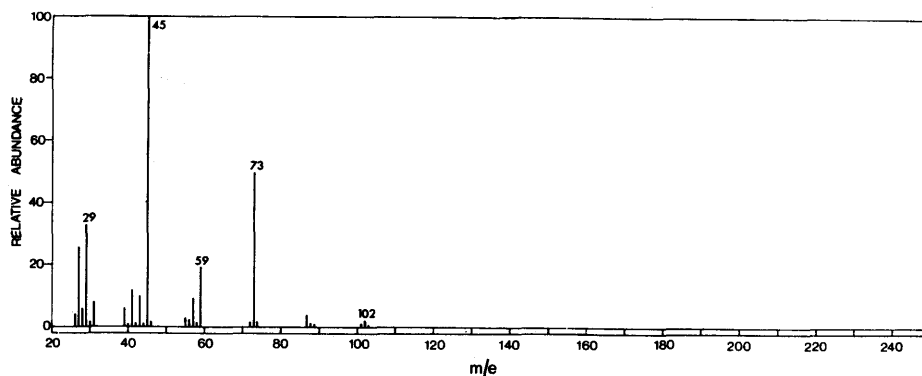
The favoured decomposition route of the molecular ion is α-cleavage. In this particular case with an unsymmetrically substituted ether α-cleavage can give rise to two ions, namely m/e 73 and m/e 87. However, the more highly substituted fragment is lost preferentially, i.e. m/e 73 more abundant than m/e 87. Further decomposition of these ions can occur with rearrangement of a hydrogen atom and elimination of a neutral ethylene molecule.
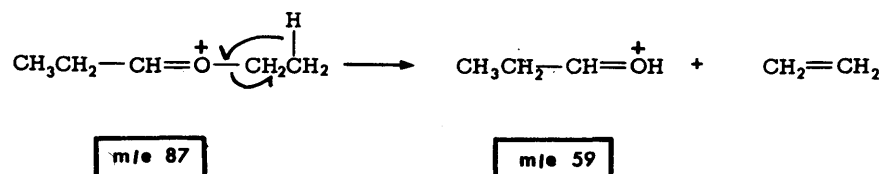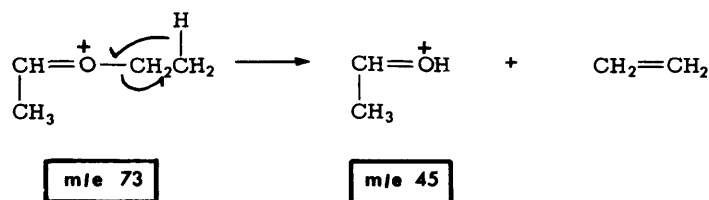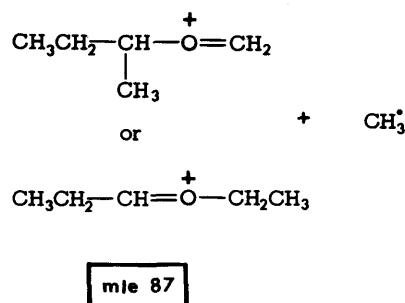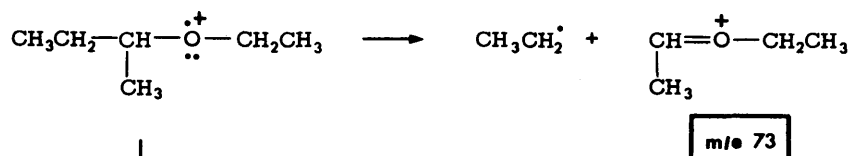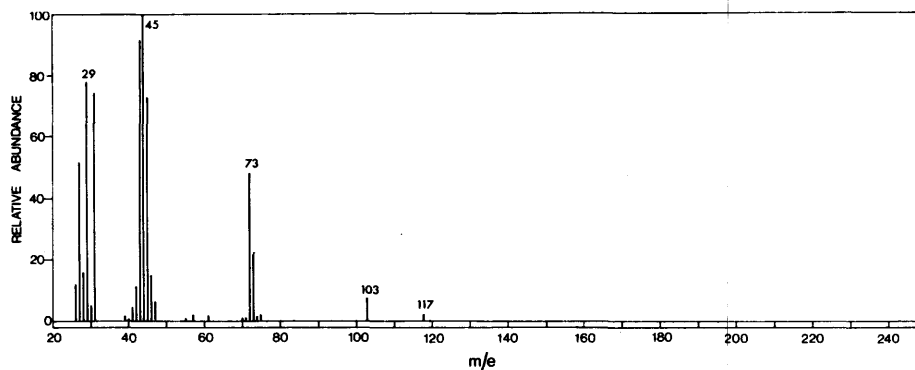
Initial α-cleavage of the molecular ion can theoretically occur in three different ways. The spectrum indicates that all three of them do infact take place i.e. m/e 117, m/e 103, and m/e 73. The loss of a hydrogen atom, m/e 117, is least favored while the elimination of an ethoxyl radical, m/e 73, is much more desirable. These ions can then undergo yet further decomposition with migration of a hydrogen atom and expulsion of a neutral ethylene molecule.
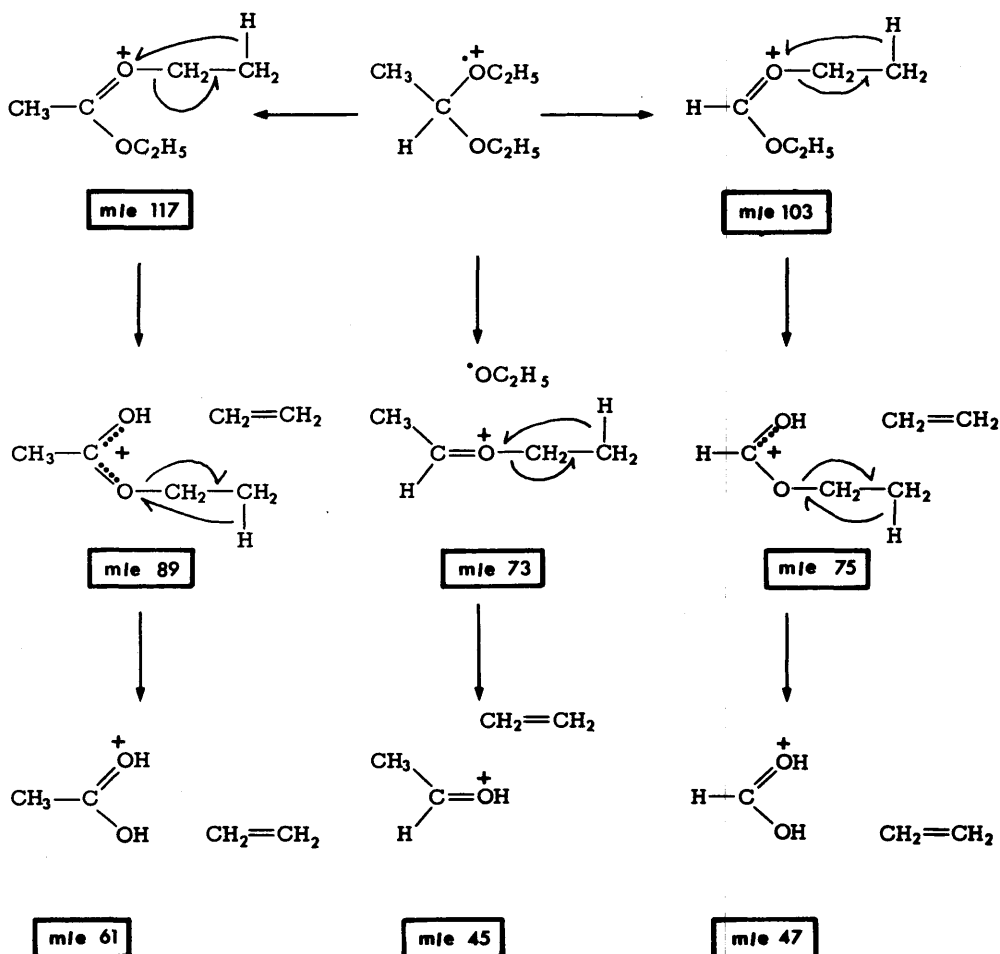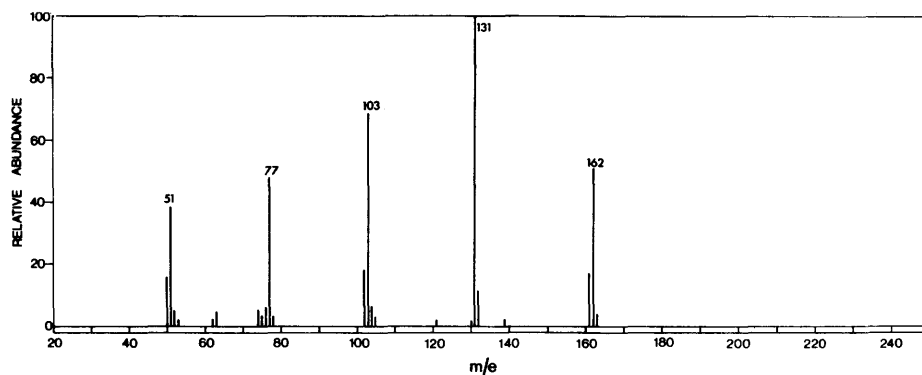
The base peak of the methyl cinnamate spectrum is at m/e 131 and is due to the loss of the methoxy radical (α-cleavage). The other two important peaks in the mass spectrum are associated with the loss of the fragments CO_2CH_3 and $CH=CHCO$.
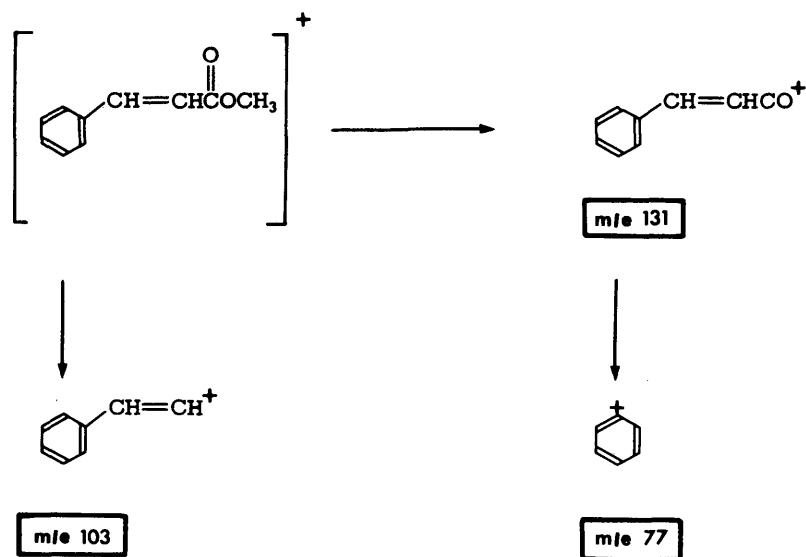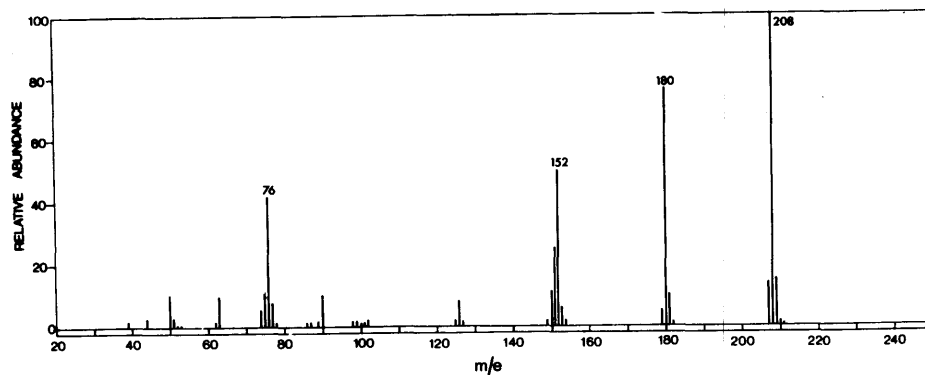
Loss of carbon monoxide is the first decomposition undergone by anthraquinone yielding **the** molecular ion of fluorenone. This followed by the loss of a second carbon monoxide molecule results in the formation of the o-biphenylene ion (m/e 152).
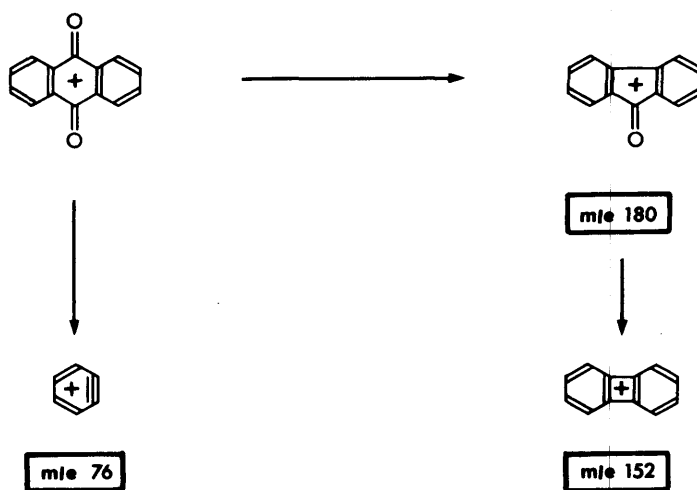
Introduction

The ultraviolet region of the spectrum extends from the lower wavelength limit of the visible region (800 – 400mμ) to 100mμ. However, instrument difficulties – absorbance of silica from which the prism is made, and absorbance of atmospheric oxygen below 190mμ effects a barrier between the near–ultraviolet (400 – 190mμ) and the far–ultraviolet (190 – 100mμ). Information about single chromophores (groups which give rise to absorption) could be obtained from the far ultra-violet, but as this is now readily obtained from infrared and nuclear magnetic resonance studies, it is still the near ultra-violet which is of most use in elucidation of molecular structure.

Whereas absorption of radiation in the infrared region (energy content ~5 Kcal/mole) is sufficient to bring about vibrational and rotational changes in molecules, absorption of radiation in the ultraviolet region (energy content ~100 Kcal/mole) causes electronic as well as vibrational and rotational changes. Because these changes occur within a narrow range the shape of the absorption band is usually broad since resolution of the electronic and associated vibrational and rotational bands is not possible.

Absorption in the near ultraviolet is indicative of the presence of unsaturated groups (normally conjugated with another unsaturated group) or of hetero-atoms with non–bonding electrons. Thus information about a molecule – as far as ultra-violet is concerned – is limited to that part of the molecule containing these groups.

Due to the absorption of ultraviolet radiation a change in the electronic energy is effected and this brings about a redistribution of the valence electrons. The energy requirements for these changes to occur is greatest for single chromophores and decreases as the number of (like or unlike) chromophores in conjunction increases. Likewise the replacement of hydrogen atoms on a chromophore by substituent groups (e.g. alkyl, methoxyl), and hence the environment of a conjugated chromophore in a molecule, has a profound effect on the energy requirements for a given electronic transition. The energy requirements are observed in a recorded spectrum by the wavelength position of the absorption band. It is on these factors, as will be seen later, that the use of ultraviolet spectroscopy is of value in structure determination.

Ultra-violet visible spectra are obtained on the one instrument as a plot of wavelength against absorbance. Wavelength is customarily recorded in wavelength (λ) units) (A – angstroms, 10^{-8} cm, or mμ, millimicrons, 10^{-7} cm). The intensity of maximum absorption is reported as the molecular extinction coefficient (ϵ) or as $\log_{10}\epsilon$, e.g. Crotonaldehyde, as recorded in ethanol solution, has an absorption maximum at 217mμ, the molecular extinction coefficient being 17,900.

This is quoted as $\lambda_{max}^{ethanol}$ 217mμ (ϵ, 17,900).

Lambert's Law

The proportion of light absorbed by a homogeneous medium is independent of the intensity of the incident light. Successive equal thicknesses of the medium accordingly reduce the intensity by successive equal fractions.

$$\log_{10} \frac{I_0}{I} = Kl$$

I_0 = Incident intensity
I = Transmitted intensity
K = Extinction coefficient
l = Thickness (cm.)

Beer's Law

The amount of light absorbed is proportional to the number of absorbing molecules through which the light passes. Thus for an absorbing solute in transparent solvent the light absorption is proportional to its concentration. Combination with Lambert's Law gives

$$\log_{10} \frac{I_0}{I} = \varepsilon cl$$

where

ε = Molecular extinction coefficient
c = Molarity

The experimentally derived $\log_{10} I_0/I$ is known as optical density (D) or absorbance (A). Most spectrophotometers read directly in absorbance.

Then

$$\varepsilon = \frac{A}{cl} \qquad \text{or} \quad \frac{MW \times A}{10c'l} \qquad \text{where } c' = g./100 \text{ ml.}$$

Where the molecular weight is unknown, the intensity of absorption is expressible as

$$E_{1\ cm.}^{1\%} = \frac{A}{c'l}$$

Hence

$$\varepsilon = E_{1\ cm.}^{1\%} \times \frac{MW}{10}$$

The Beer-Lambert relationship is as applicable to the infrared as to the ultraviolet region, although the measurement of infrared intensities is complicated by the fact that the range of wavelengths transmitted through an infrared monochromator may be of the same order as the width of the individual bands in the spectrum. Ultraviolet bands, on the other hand, are ordinarily very much wider than the wavelength range used for measurement; the incident radiation is then essentially monochromatic and the Beer-Lambert relationship is strictly obeyed.

In the visible region any colourless solvent can be employed. In the near ultraviolet region methanol, ethanol, dioxan and chloroform have transmission limits below $240 m\mu$ and are readily available. Saturated hydrocarbons such as n-hexane transmit at shorter wavelengths and can be used in thin layers to about $175 m\mu$. Although ultraviolet bands are distributed with a wide variation in intensity, the bands most useful in structural work often have $\varepsilon \approx 10000$, roughly two orders of magnitude more intense than infrared bands. Solutions are therefore extremely dilute since at 10^{-4} M, the optical density in a $1 \cdot 0$ cm. cell is $1 \cdot 0$ – a value convenient for measurement when $\varepsilon = 10^4$. The volume of solution required is of the order of 1 ml. so that $0 \cdot 1$ millimole of substance suffices, a consideration which may be of importance when only a small quantity of a natural product is available.

The cells (silica for the ultraviolet and glass for the visible), usually between 0·1 and 1·0cm. thickness, are placed between the monochromator and the detector. This is different from the practice in infrared spectroscopy where the sample is placed between the source and the mono-chromator. This arrangement in the ultraviolet case is adopted to avoid photochemical decom-position by the high energy ultraviolet radiation.
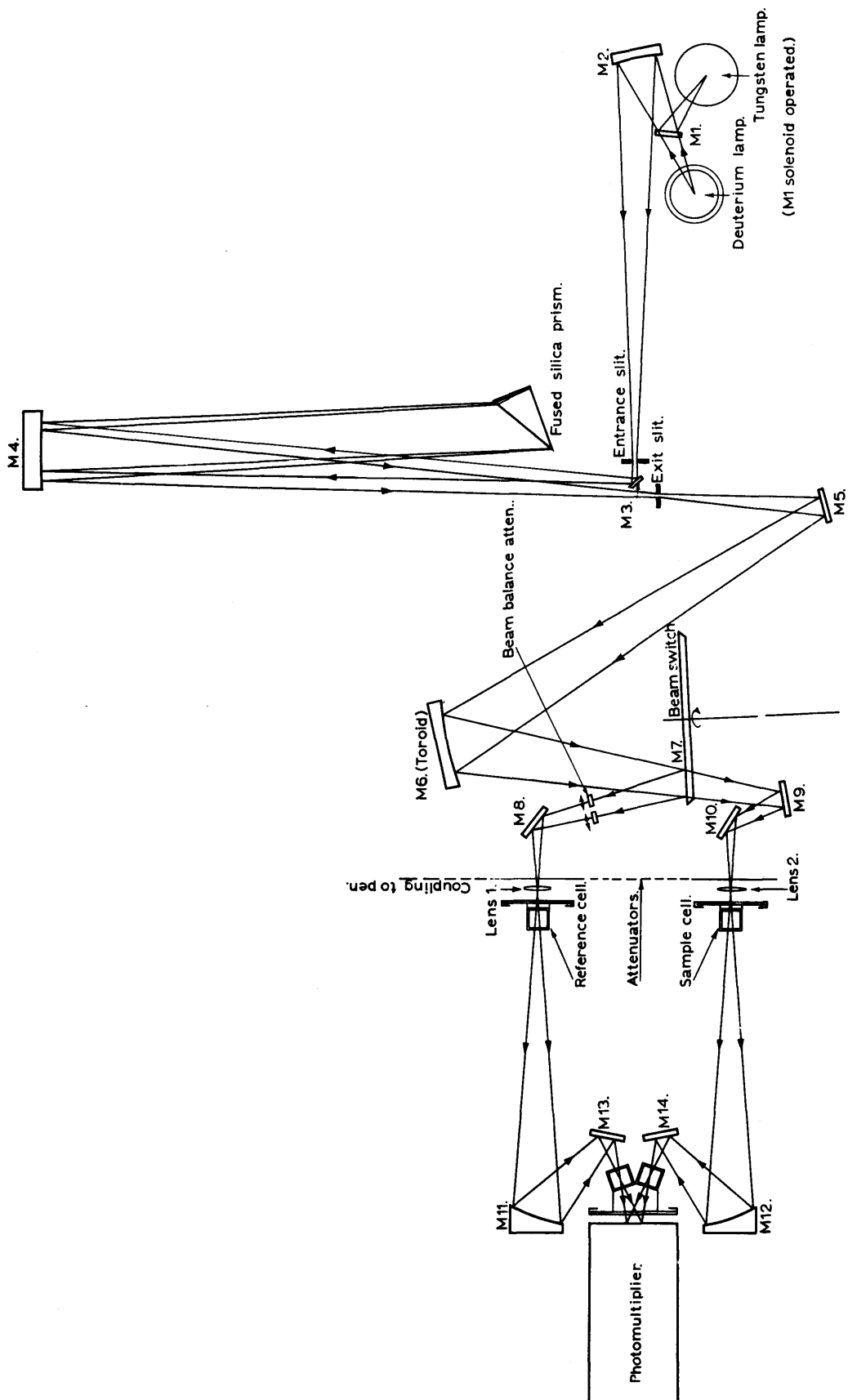
Classification of Electronic Transitions

The electronic transitions which give rise to absorption in the ultraviolet and visible regions of the spectrum fall into two main classes.

1) $\pi \rightarrow \pi^*$ transitions in which a π electron is promoted to an antibonding π orbital. These are associated with multiple bonds of carbon with carbon, nitrogen, oxygen, etc., and usually give rise to high intensity absorption.

2) $n \rightarrow \pi^*$ transitions in which a non-bonding electron (lone pair) is promoted to an antibonding π orbital. These are associated with groups such as carbonyl, thiocarbonyl, nitroso, etc., and generally give rise to low intensity absorptions.

There are other types of transitions such as $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$ but the above mentioned are by far the most important in organic chemistry.

Optical Layout of the Unicam SP.800 Spectrophotometer

M2.

M1.

Tungsten lamp.

Deuterium lamp.

(M1 solenoid operated.)

Fused silica prism.

Entrance slit.

Exit slit.

M4.

M3.

M5.

Beam balance atten.

M6. (Toroid)

M7. Beam switch

M8.

M9.

M10.

Lens 1.

Lens 2.

Coupling to pen.

Reference cell.

Attenuators.

Sample cell.

M13.

M14.

M11.

M12.

Photomultiplier.

Experimental

Obtain an unknown sample of known molecular weight.   If you are told the approximate value of ε, make up, accurately, a solution in a suitable solvent which will give an absorbance (optical density) reading of $0 \cdot 5$ on a manual instrument (e.g. Unicam SP.500) or $1 \cdot 0 - 2 \cdot 0$ on a recording instrument (e.g. Unicam SP.800 or Perkin-Elmer Model 137UV).

If the approximate ε value is not satisfied then prepare a 10^{-4} M solution and record the spectrum in a $1 \cdot 0$ cm. cell (silica).   If the absorbance is off scale either dilute accurately or use thinner cells.

From the spectrum obtained determine the wavelength(s) of the maximum absorption and molecular extinction coefficient (absorbance at λ_{max} minus absorbance of baseline).   Attempt a correlation of these values in terms of molecular structure.

The molecular extinction coefficient, $[\varepsilon]$, is a constant for a particular chromophore, but the optical density is dependent on the molecular weight of the absorbing species.

Thus

$$E^{1\%}_{1\ cm.} = \frac{10\varepsilon}{MW} \qquad \text{where} \qquad E^{1\%}_{1\ cm.} = \frac{A}{cl}$$

Hence

$$MW = \frac{10 \times \varepsilon \times c \times l}{A}$$

This principle has been applied to the determination of the molecular weight of colourless substances which form picrates (CUNNINGHAM, DAWSON and SPRING, J. Chem. Soc., 1951, 2305). Picric acid has an absorption maximum at 360mμ (ε =16000), but as this is close to the region in which more complex colourless substances absorb an arbitrarily chosen wavelength, say 380mμ, is chosen to avoid interference.

Standardise the spectrophotometer against four picrates of known molecular weights (e.g. piperidine, pyridine, triethylamine and N-ethylaniline picrates).   Use the average value of ε obtained (ca. 13000 to 14000) in the above equation for the determination of the molecular weight of a series of unknown compounds.

The Rearrangement of Phenylallyl Alcohol to Cinnamyl Alcohol

The reaction

$$Ph.CH(OH).CH=CH_2 \xrightarrow{H^+} Ph.CH=CH.CH_2OH$$
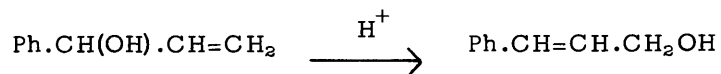
gives rise to absorption at 251mµ due to the appearance of the styrene chromophore. This can be used to calculate the rate constant at various temperatures, and the energy of activation for the rearrangement.

Method: LINSTEAD, ELVIDGE and WHALLEY, "Modern Techniques of Organic Chemistry", Butterworths, 1955, p. 176.

Chromophores

For diagnostic purposes infrared and proton magnetic resonance spectra are more reliable in identifying di- and tri-substituted double bonds, but for the tetra-substituted bond the ultra violet evidence is of first importance. The "end absorption" curve at 200-220mμ can be used as a criterion for the presence of tetra-substituted olefins, but this region is beset with experimental difficulties.

$\pi \rightarrow \pi^*$ Absorption Maxima of Ethylenic Compounds

Substitution Type	λ_{max} mμ (Heptane)	ε
$CH_2=CH_2$	162·5	15000
	174·3	5500
$R.(CH_2)_n.CH=CH_2$	~175	~13000
$R.CH\overset{t}{=}CH.R$	~180	~15000
$R.CH\overset{c}{=}CH.R$	~185	~13000
$R_2C=CH.R$	188-193	10000-13000
$R_2C=CR_2$	196-200	~10000

Conjugation reduces the energy required for the $\pi \to \pi^*$ transition, thus resulting in absorption at longer wavelengths. Acyclic dienes adopt the transoid conformation, but inclusion in a ring forces the diene to adopt a cisoid conformation which results in a bathochromic displacement (red shift) of the λ_{max} and also a lowering of the intensity to as little as one fifth of the value for an acyclic diene. These differences are of great value in structural work.

$\pi \to \pi^*$ Absorption Maxima of Dienes and Polyenes

Compound	λ_{max}	ε
	217	21000
	256	22400
	228	8500
	256	8000

The fact that diene absorption is influenced in a regular way by structure was recognised by WOODWARD (J. Amer. Chem. Soc., 1941, 63, 1123. 1942, 64, 72) whose rules, modified by FIESER (Steroids, Reinhold, New York, 1959, Ch. 1) are outlined as follows:

· Rules of Diene Absorption

Parent Heteroannular diene	214
Parent Homoannular diene	253

Add for each substituent:

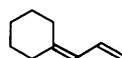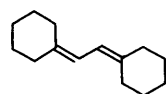|	
Double bond extending conjugation	30
Alkyl substituent, ring residue, etc.	5
Exocyclic double bond	5
N.(alkyl)$_2$	60
S.(alkyl)	30
O.(alkyl)	6
O.Ac	0

$$\lambda_{max}^{Calc} = \text{TOTAL m}\mu$$

Parent	=	214
Alkyl subst. (2x5)	=	10
λ_{max}^{Calc}	=	224 mμ (obs. 226 mμ)

Parent	=	214
Alkyl subst. (2x5)	=	10
Exo C=C	=	5
λ_{max}^{Calc}	=	229 mμ (obs. 237 mμ)

Parent	=	214
Alkyl subst. (4x5)	=	20
Exo C=C (2x5)	=	10
λ_{max}^{Calc}	=	244 mμ (obs. 247 mμ)
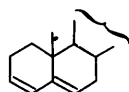
Parent	=	214
Ring residues (3x5)	=	15
Exo C=C	=	5
λ_{max}^{Calc}	=	234 mμ (obs. 234 mμ)
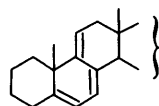
Parent	=	253
Ring residues (5x5)	=	25
Exo C=C (3x5)	=	15
C=C ext. conj.	=	30
λ_{max}^{Calc}	=	323 mμ (obs. 320 mμ)

It is of interest to note that these rules are applicable to polyenes with up to five double bonds in conjugation. The carotenoids, however, with up to eleven conjugated double bonds cannot be predicted with the above rules. The wavelength maxima can, however, be calculated by a formula developed by FIESER (J. Org. Chem., 1950, 15, 930).

$$\lambda_{max} \text{ (hexane)} = 114 + 5 \, M + n(48 \cdot 0 - 1 \cdot 7n) - 16 \cdot 5 R_i - 10 R_e$$

Here M is the number of alkyl substituents, n the total number of double bonds in conjugation and R_i and R_e are respectively the number of rings containing an endocyclic and an exocyclic double bond.

Simple acetylenes show intense absorption at $\sim 175m\mu$ ($\varepsilon \approx 6000$) which cannot be used for identification. However, conjugation of acetylenic groups produces spectra comprising a series of medium intensity peaks ($\varepsilon \approx 300$) at intervals of $\sim 2300cm^{-1}$ (the $\nu_{C \equiv C}$ in the infrared region. With more than two triple bonds in conjugation a set of high intensity ($\varepsilon \approx 10^5$) bands provide instant recognition of a polyacetylene.

En-ynes show absorption at $223m\mu$ with an inflexion at $229m\mu$; the inflexion distinguishes en-ynes from dienes.

$\pi \rightarrow \pi^*$ Absorption of Poly-ynes and En-ynes

Compound	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
Diynes						
$CH_3.C \equiv C.C \equiv CH$	227	370	236·5	390	249	210
$Et.C \equiv C.C \equiv C.Et$	227·5	360	238·5	340	253	230
Poly-ynes						
$CH_3.(C \equiv C)_4.CH_3$	234	281000	354	105	–	–
$CH_3.(C \equiv C)_6.CH_3$	384	445000	–	–	–	–
En-ynes						
$CH_2 = CH.C \equiv CH$	219	6400	228	4000	–	–
$HOCH_2.CH \overset{t}{=} CH.C \equiv CH$	223	14000	229infl	10000	–	–

Non-conjugated aldehydes and ketones show a weak intensity n→π* absorption band at about 280mμ ($\varepsilon \approx 15$) and a medium intensity π→π* absorption near 190mμ ($\varepsilon \approx 1000$). For diagnostic purposes the absorption of their 2,4-dinitrophenylhydrazones are often used.

As with dienes, αβ-unsaturated ketones and aldehydes have an intense (solvent variable) π→π* absorption band in the accessible region (upwards of 220mμ) of the spectrum. The n→π* band now appears at 310-350mμ (ε 50-100). Rules are available for the calculation of λ_{max}, but it should be noted that as applied to αβ-unsaturated aldehydes the rules do not give good agreement with the observed values.

Absorption Maxima of Carbonyl Compounds

Compound	π→π* band		n→π* band	
	λ_{max}	ε	λ_{max}	ε
$CH_3.CO.CH_3$	188	1860	279	13
Cycohexanone	–	–	285	14
$CH_3.CHO$	193	–	292	15
$CH_2=CH.CHO$	208	10000	328	13
$(CH_3)_2C=CH.CO.CH_3$	235	14000	314	6
Cyclohexenone	224	10300	–	–

Calculation of λ_{max} mμ [EtOH]

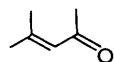|	
Parent acyclic and 6-membered enone	215
Parent cyclopentenone	202
Parent $\alpha\beta$-unsaturated aldehydes	207

$$\underset{\delta}{\overset{\delta}{\diagdown}}C = C - C = C - C = O$$
$$\gamma\beta\alpha$$
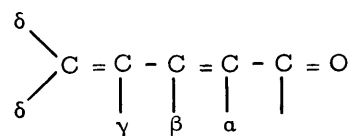
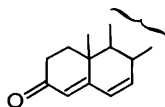| Add for each substituent:	α	β	γ	δ
Alkyl or ring residue	10	12	18	18
$O.CO.CH_3$ or $O.CO.C_6H_5$	6	6	6	6
OH	35	30	–	50
OAlkyl	35	30	17	31
Br	25	30	–	–

Add for:

Exocyclic double bond	5
Double extending conjugation	
(a) heteroannular	30
(b) homoannular	68

Parent $\qquad$ = 215
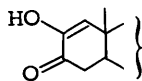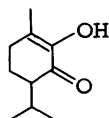Subst. 2β $\qquad$ = 24

λ_{max}^{EtOH} (calc.) = 239 mμ (obs. 237 mμ)

Parent $\qquad$ = 215
Subst. 1β $\qquad$ = 12
$\qquad$ 1δ $\qquad$ = 18
Exo C=C $\qquad$ = 5
C=C ext. conj. $\qquad$ = 30

λ_{max}^{EtOH} (calc.) = 280 mμ (obs. 283 mμ)

Parent $\qquad$ = 215
Subst. 1β $\qquad$ = 12
α-OH $\qquad$ = 35

λ_{max}^{EtOH} (calc.) = 262 mμ (obs. 270 mμ)

Parent $\qquad$ = 215
Subst. 2β $\qquad$ = 24
α-OH $\qquad$ = 35

λ_{max}^{EtOH} (calc.) = 274 mμ (obs. 274 mμ)
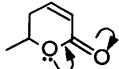
Parent $\qquad$ = 202
Subst. 1β $\qquad$ = 12

λ_{max}^{EtOH} (calc.) = 214 mμ (obs. 218 mμ)

Parent $\qquad$ = 202
Subst. 1α $\qquad$ = 10
$\qquad$ 2β $\qquad$ = 24
Exo C=C $\qquad$ = 5

λ_{max}^{EtOH} (calc.) = 241 mμ (obs. 241 mμ)

$\pi \rightarrow \pi^*$ Absorption Maxima of Unsaturated Acids and Related Compounds

Compound	λ_{max} mμ	ε
$CH_2=CH.CO_2H$	200	10000
$CH_3.CH\overset{t}{=}CH.CO_2H$	205	14000
$CH_3.CH\overset{t}{=}CH.CO_2CH_3$	205	16500
	205	10700

The above class of compounds absorb at much shorter wavelengths than the corresponding enones because the electron affinity of the carbonyl group is reduced by the interaction shown above thus increasing the energy of the transition. The position of λ_{max} for αβ-unsaturated acids may be predicted with fair accuracy. (NIELSON, J. Org. Chem., 1957, 22, 1539).

	mμ in EtOH
Mono-substituted α or β	208 ± 5
Di-substituted αβ or ββ	217 ± 5
Tri-substituted αββ	225 ± 5

For each exocyclic double bond or double bonds endocyclic to a 5- or 7-membered ring add 5mμ.

The spectrum of benzene shows no resemblance to that of hexa-1,3,5-triene and has bands at 255mμ ($\epsilon = 230$), 200mμ ($\epsilon = 8000$) and 185mμ ($\epsilon = 60000$). The effect of substituents on the spectrum of benzene have been extensively studied. Alkyl and alkenyl substituents cause a bathochromic shift (red shift). With polar substituents, e.g. $-NR_2$, $-OH$, etc., which allow for the p→π conjugation and $>C=O$ and $-NO_2$ where polarizability is of importance, absorption due to electron transfer transitions is apparent. These two types of transfer can be expressed as shown below.
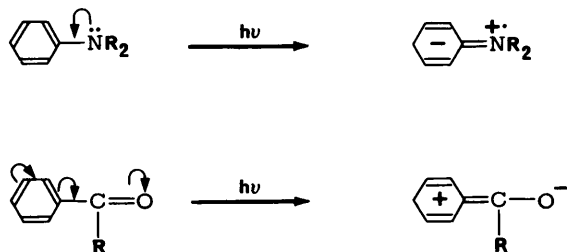
In heterocyclic chemistry model compounds are essential for the interpretation of most spectra. No rules are available for the prediction of the wavelength maxima of aromatic compounds except in the case of aromatic carbonyl compounds where acetophenone is taken as the parent chromophore, and increments alloted on the usual basis (SCOTT, Experientia, 1961, 17, 68).

Electron Transfer Absorption of Substituted Benzenes
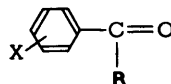
Calculation of λ_{max}		mμ in EtOH	
Parent chromophore:			
R = Alkyl or ring residue		246	
OH or OAlkyl		230	
H		250	
Add for each substituent X:	o-	m-	p-
Alkyl or ring residue	3	3	10
OH or OAlkyl	7	7	25
$O^{\ominus}$	11	20	78
Cl	0	0	10
Br	2	2	15
NH_2	15	15	58
NHAc	20	20	45
$N(Alk)_2$	20	20	85

Parent		=	246
Substituents			
o-ring residue		=	3
o-methyl		=	3
m-bromo		=	2
	λ_{max}^{Calc}	=	254 mμ (obs. 254 mμ)
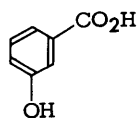
Parent		=	230
Substituent			
m-hydroxy		=	7
	λ_{max}^{Calc}	=	237 mμ (obs. 236 mμ)
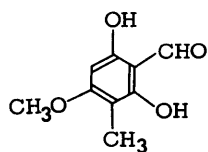
Parent		=	250
Substituents			
o-hydroxy (2)		=	14
m-methyl		=	3
p-methoxy		=	25
	λ_{max}^{Calc}	=	292 mμ (obs. 295 mμ)

	λ_{max}	approx. ε	Solvent
Benzene	200	8,000	H
	255	230	
Toluene	261	300	H
Xylenes	266	400–800	H
Diphenylmethane	262	490	A
Diphenyl	250	18,000	A
Styrene	244	12,000	A
	282	450	
Stilbene (trans)	295	27,000	A
(cis)	280	13,500	
Acetophenone	240	13,000	A
	278	1,100	
	319	50	
Benzaldehyde	244	15,000	A
	280	1,500	
	328	20	
Benzoic acid	230	10,000	W
	270	800	
Cinnamic acid	273	20,000	A
Benzophenone	252	20,000	A
	325	180	
Nitrobenzene	252	10,000	H
	280	1,000	
	330	125	
Phenol	210·5	6,200	W
	270	1,450	
Phenol (anion)	235	9,400	aq.OH$^-$
	287	2,600	
Phenyl acetate	263	500	
Aniline	230	8,600	W
	280	1,430	
Aniline (cation)	203	7,500	aq.H$^+$
	254	160	
Acetanilide	242	14,400	A
	280	500	
Furan	200	10,000	H
Pyrrole	210	16,000	H
	340	300	
Pyridine	195	7,500	H
	250	2,000	
Quinoline	275	4,500	H
	311	6,300	
Isoquinoline	262	3,700	H
	317	3,500	
Acridine	252	10,000	A
	347	8,000	
		$\log \varepsilon$	
Naphthalene	220	5·05	A
	275	3·75	
	314	2·50	
Anthracene	250	5·20	A
	380	3·90	
Pentacene (blue)	580	4·10	A
Tropolone	247	4·82	H
	331	4·51	
	380	4·14	
Tropone	225	4·34	iso-octane
	297	3·74	
	310	3·67	

Interpretation of Spectra

In this section six typical ultraviolet spectra are discussed in terms of molecular structure. However, in practice the ultraviolet spectrum of a compound would be recorded in conjunction with its infrared and proton magnetic resonance spectrum in an attempt to deduce its molecular structure. It has been assumed, therefore, that the functional groups have been detected and we shall be concerned in assigning substitution patterns.

All spectra were recorded as solutions in ethanol (solvent-solvent base line shown as dotted line) on a Unicam SP.800B ultraviolet-visible spectrophotometer. For convenience absorption maxima and ε values are shown on each spectrum.
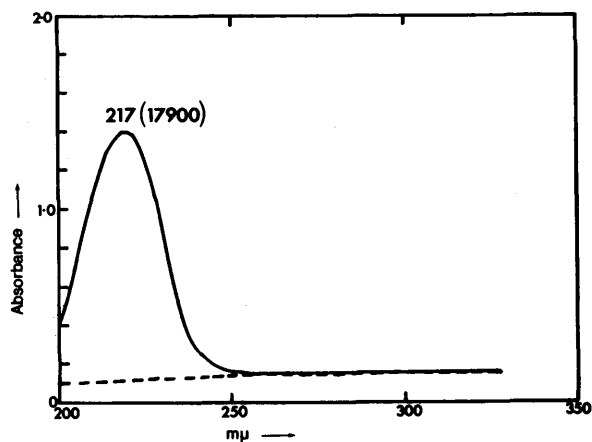
This spectrum shows one absorption band at 217mµ ($\epsilon = 17900$) which can be assigned to an αβ-unsaturated aldehyde or ketone. A diene can be ruled out since only butadiene itself (λ_{max} = 217mµ, $\epsilon = 21000$) absorbs below 220mµ.

If an αβ-unsaturated ketone is considered only a vinyl ketone such as methyl vinyl ketone (λ_{max} = 219mµ, $\epsilon = 3600$) can be considered, but the ϵ value for this type of compound is about 5000.

Thus we are led to assign this spectrum to a mono-substituted αβ-unsaturated aldehyde, either α- or β-substituted, for which the calculated values of λ_{max} are 217mµ and 219mµ.
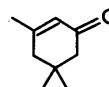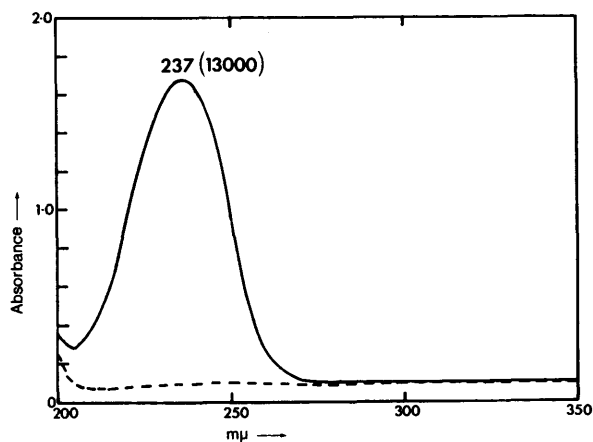
Assuming a diene has been ruled out, this spectrum can be assigned to one of the following possibilities:

βββ-disubstituted acyclic enone
β-substituted cyclohexenone
αββ-trisubstituted cyclopentenone

Recourse to the infrared spectrum would have to be made for a final decision.
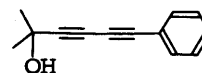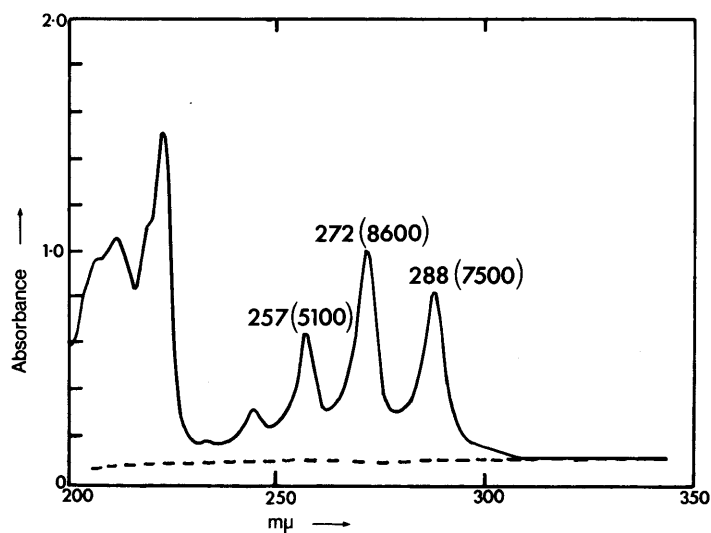
This spectrum illustrates the typical band pattern associated with poly-ynes. Note the peak separation of ca. 2300cm^{-1}. The strong absorption in the 220mμ region is due to benzenoid absorption. Conjugation of the diacetylene with the benzene ring causes a bathochromic shift of all the poly-yne bands together with an enhancement of the intensity of the absorptions.
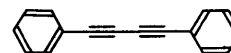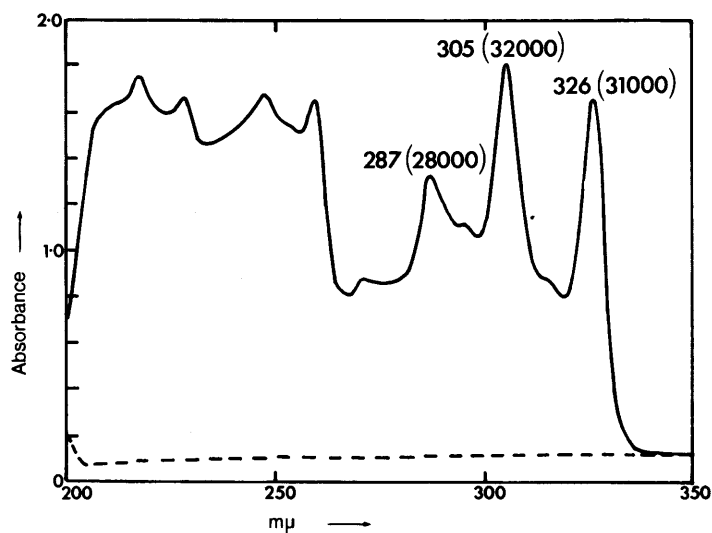
This spectrum, like the preceding example, shows the characteristic poly-yne bands and regular peak separation. Conjugation with the two benzene rings causes a further bathochromic shift and a substantial increase in intensity.
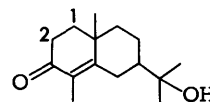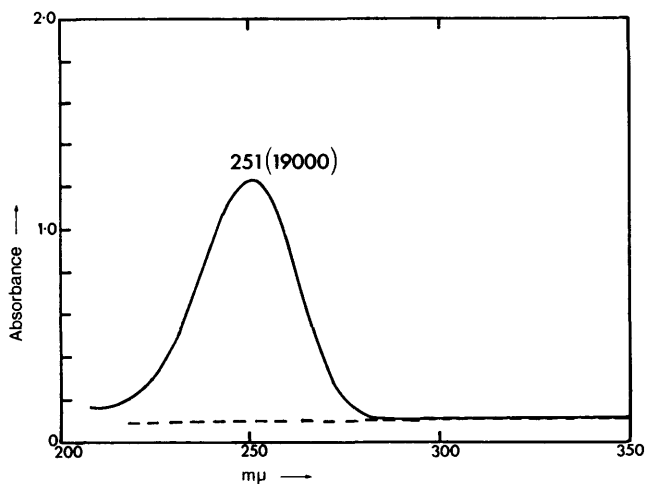
Absorption at 251mμ in an αβ-unsaturated ketone would require at least αββ-trisubstitution (215 +10 + 24 = 249mμ) in an acyclic enone or cyclohexenone. Addition of 5mμ, the increment for an exocyclic double bond gives a final calculated value of 254mμ which is in good agreement with the above structure. The observed value rules out the possibility that the double bond is between C_1 and C_2 (λ_{max} calc. = 215 + 12 = 227mμ) and also that the enone is not present in a five membered ring (λ_{max} calc. = 202 + 10 (α-CH$_3$) + 24 (2β ring residues) + 5 (exo C=C) = 241mμ).
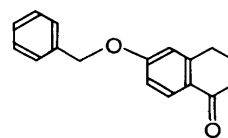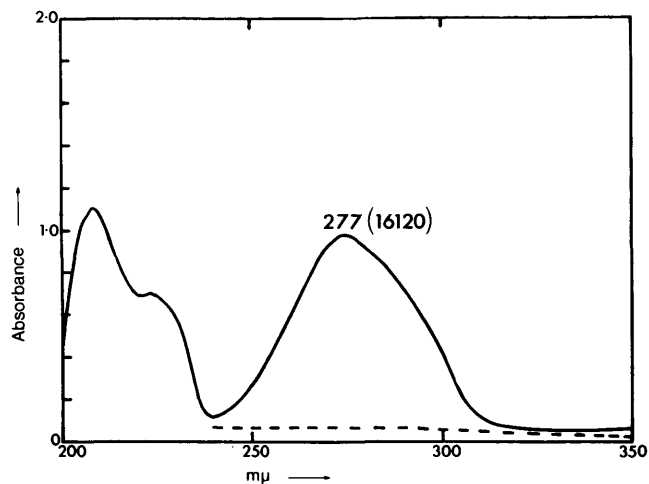
This spectrum shows benzenoid absorption (π→π*) at 208 and 225mμ, an electron transfer band at 277mμ (ε = 16120), and a weak carbonyl n→π* band as a shoulder at about 300mμ. The electron transfer band is in good agreement with the calculated value (246 + 3 (o-ring residue) + 25 (p-benzyloxy) = 274mμ) for this compound and rules out the other possible product of oxidation of 2-benzyloxytetralin, namely 7-benzyloxytetralone-1 (λ_{max} calc. = 246 + 3 (o-ring residue) + 7 (m-benzyloxy) = 256mμ).

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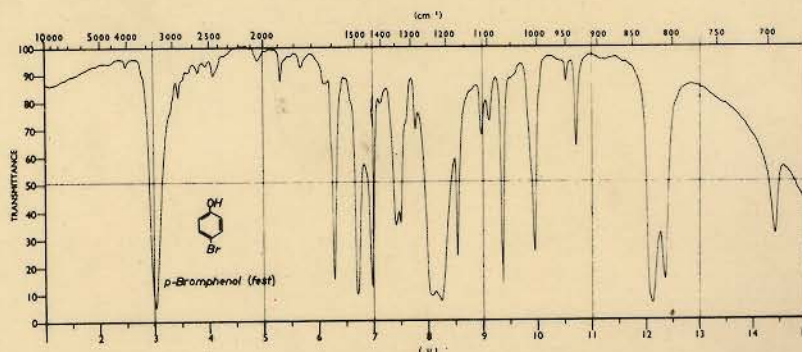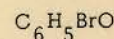
All spectra were recorded linearly in wavelength, but for convenience the major bands have been given in wavenumbers, together with their relative intensities.

Serial No: 159

p-Bromophenol

C_6H_5BrO

State: Cryst. between NaCl plates

Concentration:

Thickness: Capillary

Temperature:

B.P.: $132^\circ C/15mm$

M.P.: $64^\circ C$

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p-Bromophenol (fest)

I	cm⁻¹
10	3360
1	2930
1	2530
1	1895
9	1592
10	1493
9	1435
2	1405
7	1351
3	1335
10	1289
10	1244
8	1217
3	1175
3	1116
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4	951
10	935
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